DOCUMENT RESUME

ED 052 921   SE 009 206

AUTHOR   Holden, Alan
TITLE   Bonds Between Atoms.
INSTITUTION   Bell Telephone Labs., Inc., Murray Hill, N.J.
PUB DATE   66
NOTE   82p.
AVAILABLE FROM Bell Telephone Laboratories, Murray Hill, N. J.

ABSTRACT
        The field of inquiry into how atoms are bonded
together to form molecules and solids crosses the borderlines between
physics and chemistry encompassing methods characteristic of both
sciences. At one extreme, the inquiry is pursued with care and rigor
into the simplest cases; at the other extreme, suggestions derived
from the more careful inquiry are pushed to provide qualitative
insights into the complexities of chemical behavior. This monograph
provides an introduction to both points of view and to the
relationship between them. Primary emphasis is on the physical nature
of the simplest chemical bonds, though it examines a few molecules
that are more complicated to point out the wide qualitative relevance
of the more rigorous approach. Extensive use of simplified models is
made. (Author/RH)

GENERAL PREFACE

This monograph was written for the Conference on the New Instructional Materials in Physics, held at the University of Washington in the summer of 1965. The general purpose of the conference was to create effective ways of presenting physics to college students who are not preparing to become professional physicists. Such an audience might include prospective secondary school physics teachers, prospective practitioners of other sciences, and those who wish to learn physics as one component of a liberal education.

At the Conference some 40 physicists and 12 filmmakers and designers worked for periods ranging from four to nine weeks. The central task, certainly the one in which most physicists participated, was the writing of monographs.

Although there was no consensus on a single approach, many writers felt that their presentations ought to put more than the customary emphasis on physical insight and synthesis. Moreover, the treatment was to be "multi-level" --- that is, each monograph would consist of several sections arranged in increasing order of sophistication. Such papers, it was hoped, could be readily introduced into existing courses or provide the basis for new kinds of courses.

Monographs were written in four content areas: Forces and Fields, Quantum Mechanics, Thermal and Statistical Physics, and the Structure and Properties of Matter. Topic selections and general outlines were only loosely coordinated within each area in order to leave authors free to invent new approaches. In point of fact, however, a number of monographs do relate to others in complementary ways, a result of their authors' close, informal interaction.

Because of stringent time limitations, few of the monographs have been completed, and none has been extensively rewritten. Indeed, most writers feel that they are barely more than clean first drafts. Yet, because of the highly experimental nature of the undertaking, it is essential that these manuscripts be made available for careful review

by other physicists and for trial use with students. Much effort, therefore, has gone into publishing them in a readable format intended to facilitate serious consideration.

BONDS BETWEEN ATOMS

FOREWORD

The field of inquiry into how atoms are bonded together to form mole-
cules and solids crosses the borderlines between physics and chemistry,
encompassing methods characteristic of both sciences. At one extreme,
the inquiry is pursued with care and rigor into the simplest cases; at
the other extreme, suggestions derived from the more careful inquiry
are pushed with daring to provide qualitative insights into the com-
plexities of chemical behavior.

This monograph provides an introduction to both points of view and
to the relationship between them. Dealing primarily with the physical
nature of the simplest chemical bonds, it nevertheless examines a few
molecules that are much more complicated, in order to point out the
wide qualitative relevance of the more rigorous approach.

In developing its subject the monograph makes extensive use of
simplified models. Indeed, taken as a whole, it constitutes an exer-
cise in model making. It offers the lesson that, in conducting such an
activity, a difficult balance must be achieved between a sense of ad-
venture on the one hand and a sense of responsibility on the other. The
adventure is found in inventing the models and employing them in wide
contexts. The responsibility resides in pursuing their implications
relentlessly, to the point of calculating numerical values with their
aid and comparing those values with the results of experimental meas-
urements.

Alan Holden

C O N T E N T S

outlines the early history of speculation on the
way matter is put together, and the origin of the
electrostatic explanation of bonding that is used
today.

describes qualitative differences between various
forms of matter and correlates them with a classi-
fication of bonds into four conventional types and
mixtures of those types.

examines more quantitatively those bonds which
can be explained in the simplest classical terms:
the electrostatic interactions between oppositely
charged ions.

discusses the weak binding forces between such
inert atoms as argon--forces that form an ingre-
dient of all binding but are usually masked by
stronger forces.

approaches the problem of explaining the covalent
bond by examining simplified models of its sim-
plest case, the hydrogen molecule-ion.

shows how to revise the ideas of the previous
chapter to suit the more usual case of a covalent
bond formed by two electrons.

"The Parts of all homogeneal hard Bodies which fully touch one another, stick together very strongly. And for explaining how this may be, some have invented hooked Atoms, which is begging the Question . . . I had rather infer from their Cohesion, that their Particles attract one another by some Force, which in immediate Contact is exceeding strong, at small distances performs the chymical Operations above-mentioned and reaches not far from the Particles with any sensible Effect . . . There are therefore Agents in Nature able to make the Particles of Bodies stick together by very strong Attractions. And it is the Business of experimental Philosophy to find them out." So wrote Sir Isaac Newton two hundred sixty years ago.

The pursuit of Sir Isaac's Business over a quarter millenium has progressively found them out, wholly verifying the remarkable insight of that remarkable man. In 1945 Erwin Schroedinger, the principal architect of the means for completing the verification, could write that "the atoms forming a molecule, whether there be few or many of them, are united by forces of exactly the same nature as the numerous atoms which build up a true solid, a crystal." We know today that those forces are primarily electrostatic, the forces of attraction between electrical charges of opposite sign. The gravitational and magnetic forces that also operate in these unions are entirely negligible in comparison with the electrostatic.

In view of how little was known about atoms in Newton's time, his insight seems the more remarkable. Speculative minds had promulgated atomic theories of one sort and another for two thousand years. But Robert Boyle, Newton's contemporary, had been the first to urge the view that the world is made of <u>compounds</u>

that can be decomposed into <u>elements</u>. The "elements" of earlier times were not separate kinds of ultimate, un-decomposable matter; they were aspects of a single neutral substance of which the world was made. Those different aspects were produced by the combined application of definite and disting-uishable formative principles on the neutral substance.

These ideas about the world arose from a doctrine of Aristotle that em-phasized the distinction between "sub-stance" and "form."[1] The doctrine recognized four formative principles: hotness and dryness and their oppo-sites, coldness and wetness. By im-pressing those qualities in pairs on the single substance, the four primal forms of matter are produced according to the following scheme:

$$\text{dryness} + \text{hotness} \rightarrow \text{fire}$$
$$\text{dryness} + \text{coldness} \rightarrow \text{earth}$$
$$\text{wetness} + \text{hotness} \rightarrow \text{air}$$
$$\text{wetness} + \text{coldness} \rightarrow \text{water}$$

The many subsidiary differences be-tween the forms in which these four elements appear are reflections of the differences in the proportions and intensities with which the formative principles are applied.

Of all the ancient speculations about the construction of the world, this doctrine of the Four Elements gave an especially powerful impulse and direction to early chemistry. The Arabs absorbed the doctrine when they conquered Egypt in the seventh cen-tury, using it to interpret the ex-

---

[1] It has been suggested that Aristotle may have arrived at his doctrine by reflecting upon the activities of craftsmen and artists, who trans-mute formless matter into the objects that are of interest and use to man. Notice in any case that the Latin word <u>materia</u> meant wood-for-building.

periments stimulated by their active
spirit of enquiry. The alchemy that
developed at their hands rested on
their belief that they could change
any kind of matter into any other if
they could but discover what forma-
tive principle, applied in what man-
ner to the first kind, would produce
the second.

The winning and modification of
metals was an especially important
preoccupation of the early investiga-
tors. Outstanding among them was Jabir
ibn Hayyan (the "Geber" of certain
Latin texts) who added two more ele-
ments, mercury and sulfur, to the
primal four. "Mercury" was the princi-
ple giving metals their unalterable
property, and "sulfur" was the earthly
impurity from which they could be
cleansed. With increasing attention
to the preparation of substances for
medical use, a third element was
added to the new list: "salt," the
residue that remained fixed after cal-
cination. Indeed these three formed
the tria prima of Paracelsus, the vi-
olent[2] and peripatetic man whose ex-
ample inspired the reckless pharma-
cological expermentation of the six-
teenth century.

As has happened so often in the
history of science and as happens to-
day, without doubt, a body of theory
later overthrown stimulates and organ-
izes much valid observation of nature.
When Boyle undertook his experiments
in the middle of the seventeenth cen-
tury, he could profit from the re-
corded results of many centuries of
chemical work. Contemplating them, he
wrote the "Sceptical Chymist," pub-
lished in 1661, which raised serious
objections to the tria prima:

> There are some bodies from which
> it has not yet been made to appear
> that any degree of fire can separ-

ate either salt, or sulfur, or
mercury, much less all three. Gold
may be heated for months in a fur-
nace without losing weight or alter-
ing, and yet one of its supposed
constituents is volatile and an-
other combustible. Neither can
solvents separate any of the three
principles from gold; the metal
may be added to, and so brought
into solution . . . but the gold
particles are present all the
time; and the metal may be reduced
to the same weight, of yellow,
ponderous malleable substance it
was before.

After calling the tria prima in
question in this fashion, Boyle pro-
posed an alternative picture of chem-
ical occurrences. He remarked upon
the fact that many metals - lead and
copper, for example - may be dissolved
in acids and their properties entirely
disguised in the resulting compound.
Meeting with corpuscles of another
kind, the corpuscles of metal may be
more disposed to unite with them, he
suggested, than to join with the par-
ticles forming the original metallic
cluster. Thus from the coalition of
two different corpuscles a new body
may be formed "as really one as either
of the corpuscles before they were
confounded."

It was bold to suggest that mer-
cury, a silvery metallic liquid, and
sulfur, a readily fusible yellow
solid, should combine to form the
red mineral cinnabar, rather than the
yellowish metal, gold. Indeed it seems
equally bold today to advance the idea
that the entire richness and diversity
of the material world is formed by
union of only a hundred kinds of
atomic particles. Our notion that
water is made from the particles of
two gases, hydrogen and oxygen, in
two-to-one proportion may seem no less
preposterous than Aristotle's notion
that water represents the impress of
wetness and coldness on a matter-stuff,
or than the notion of Thales of Mile-
tus that water is itself the sole ele-

---

[2] On receiving the professorship of medicine at
Basle, Paracelsus' first public act was to burn
the great handbooks of medicine by Galen and
Avicenna.

mentary source of the world.[3] But we
have vastly more evidence to support
today's fantastic contention than did
the ancients. That evidence is the
major content of the chemical knowl-
edge acquired over the past three cen-
turies.

But Boyle had left unanswered -
in fact unstated - the question,
"Why and when do the particles join?"
It was appropriate that Newton, who
had made especially vivid use of the
idea of force in the mechanics of
visible objects, and who had fathered
the law of universal gravitation,
should appeal to the idea of force
again to explain the cohesion of in-
visible particles in solids and also
the interchanges of their allegiance
in chemical reactions. But some good
quantitative feeling, or perhaps some
rough calculation that he does not
describe, warned him that gravita-
tional forces between the particles
could not provide the explanation that
he sought.

The electrostatic explanation
that we accept today had to await the
experiments with electricity that form
a conspicuous scientific ornament of
the nineteenth century. The previous
century had witnessed a few notable
discoveries, in particular that of the
two kinds of electricity, positive and
negative, by Charles Dufay in 1734.
Dufay's observation that bodies with
like electrification repel each other
while those with unlike electrifica-
tion attract each other had been made
quantitative by Charles-Augustin
Coulomb's brilliant use of his tor-
sion balance near the end of the
eighteenth century. But it was Ales-
sandro Volta's announcement in 1800
of his electric battery, "which in a

word provides an unlimited charge or
imposes a perpetual action or impul-
sion on the electric fluid," that made
possible the crucial chemical experi-
ments.

In that same year William Nichol-
son noticed the products of electroly-
sis of river water appearing at the
free ends of wires connected to a
voltaic pile. Hence one of the first
acts of Sir Humphry Davy, on becoming
director of the laboratory at the
Royal Institution in London the fol-
lowing year, was to construct a large
battery of the sort Volta had de-
scribed. With it he followed up Nichol-
son's observation vigorously over the
next five years, with results that he
summarized in the following words.

> Hydrogen, the alkaline substances,
> the metals, and certain metallic
> oxides are attracted by negatively
> electrified metallic surfaces and
> repelled by positively electrified
> metallic surfaces; and contrari-
> wise, oxygen and acid substances
> are attracted by positively elec-
> trified metallic surfaces and re-
> pelled by negatively electrified
> surfaces; and these attractive and
> repulsive forces are sufficiently
> energetic to destroy or suspend the
> usual operation of elective affin-
> ity.

It was then natural to assume
further that "the usual operation of
elective affinity" is itself electro-
static - the attraction of oppositely
charged atoms of different species.
Davy in England, and Jöns Berzelius in
Sweden, both soon came to this view,
and the latter formulated an electro-
chemical theory of the formation of
compounds, published in 1814, which
put forward this "dualistic hypothesis"
in explanation of all chemical action.
Berzelius even extended these ideas
into organic chemistry, proposing that
groups of atoms can form compound "radi-
cals," positive and negative, which
then join together as elements would.

But it is clear that, however

---

[3] In a famous experiment the seventeenth century
Belgian physician and chemist, Jean Baptiste van
Helmont, believed that he had verified Thales'
doctrine by growing a willow shoot in dried
earth and watering it regularly until it had
gained many pounds in weight without receiving
any other nutrient that van Helmont could dis-
cern. Ironically, this was the man who also dis-
covered carbon dioxide, in other experiments.

well such a theory may fit the obser-
vations on substances that can be
brought into solution and electrolyzed,
it cannot explain all the interatomic
forces found in nature. From measure-
ments on gaseous hydrogen and oxygen
and their reaction to form water vapor
it was becoming increasingly clear in
Berzelius' own time that these gases
are both composed of molecules of
which each contains two atoms tightly
joined. Berzelius long opposed this
conclusion because he could not find
in his dualistic theory any binding
force between two identical atoms.
But the idea of diatomic molecules
was unavoidable - and binding force
there must be.

The origin of the forces between
identical atoms has been found only in
this century, with the identification
of the electron by J. J. Thomson in
1897 and the development of pictures
of the inner structure of atoms made
possible by that discovery. It turns
out that such seemingly diverse inter-
atomic attractions as those found in
hydrogen molecules, in metals, and in
crystalline argon can all be convinc-
ingly explained in electrostatic terms.
The next chapter will provide a quali-
tative discussion of the various ways
in which the electronic constitution
of atoms can operate to provide bonds
between them, and the rest of this
monograph will pursue the same ques-
tions more quantitatively and in
greater detail.

In talking about interatomic bonds, and about the aggregations of atoms assembled by them, it is helpful to make classifications - suggestive, not hard and fast - of as many sorts as come to mind. The bonds might be divided, for example, into two classes; those between similar atoms, such as the bond between two hydrogen atoms which ties them together in a hydrogen molecule, and those between dissimilar atoms, such as the bond between sodium and chlorine in sodium chloride. And the world's solids might be divided into two classes: those which melt into electrically conducting liquids, and those which melt into electrically insulating liquids. The proposed classification of interatomic bonds is clearly exhaustive; the classification of solids is not, for many solids decompose into new materials at temperatures below their melting point. But these classifications are simple, and useful for a start.

If two atoms come close to each other, they will not remain unaffected by each other. If they belong to different atomic species, one may accommodate electronic charges somewhat more readily than the other. Charge may flow from the one to the other, leaving the one with a net positive charge and giving the other a net negative charge. Then the two partly ionized atoms will attract each other electrostatically, providing the bond visualized by Davy and Berzelius as the last chapter described. In the extreme case each atom of one species completely transfers one electron to an atom of the other species, and the ions can be expected to assemble about one another in such a way that each ion is as near as it can be to as many ions of the other species as possible, and as far as possible from the similarly charged ions of its own species.

In such a case an ion has no

preference for a particular one of the ions of the other species. Molecules, formed by pairs of ions, cannot be unambiguously identified in the solid. In crystalline sodium chloride, for example, the ions are arranged as shown in Fig. 2.1 (see next page): each ion is immediately surrounded by six ions of the other species.

As that figure shows, the ions in such a solid are packed together too tightly to move past one another; they can only vibrate about their average positions. But when the solid is melted, the ions will be able to drift through the liquid as they could not through the solid. If an electric field is applied to the liquid, the ions of the two species will drift in opposite directions. When they reach the electrodes that establish the field, the negative ions will discharge their extra electrons to the positively charged electrode, and the positive ions will acquire from the negative electrode the electrons that they lost when they became ions.

In this way neutral atoms of the two species will accumulate at the opposite electrodes; and if they cannot combine with the material of the electrode, they will combine with one another in whatever way is characteristic of them. Molten sodium chloride, for example, can be electrolyzed to yield sodium metal and chlorine gas. Since the drifting of the ions carries a drift of charge, a current flows; and the amounts of metal and gas produced are proportional to the product of the current by the time during which it has flowed. Thus, in principle at least, the fact that a solid is ionically bonded can be ascertained by observing that it is an electrical insulator that melts to an electrically conducting liquid whose conduction is accompanied by electrolysis.
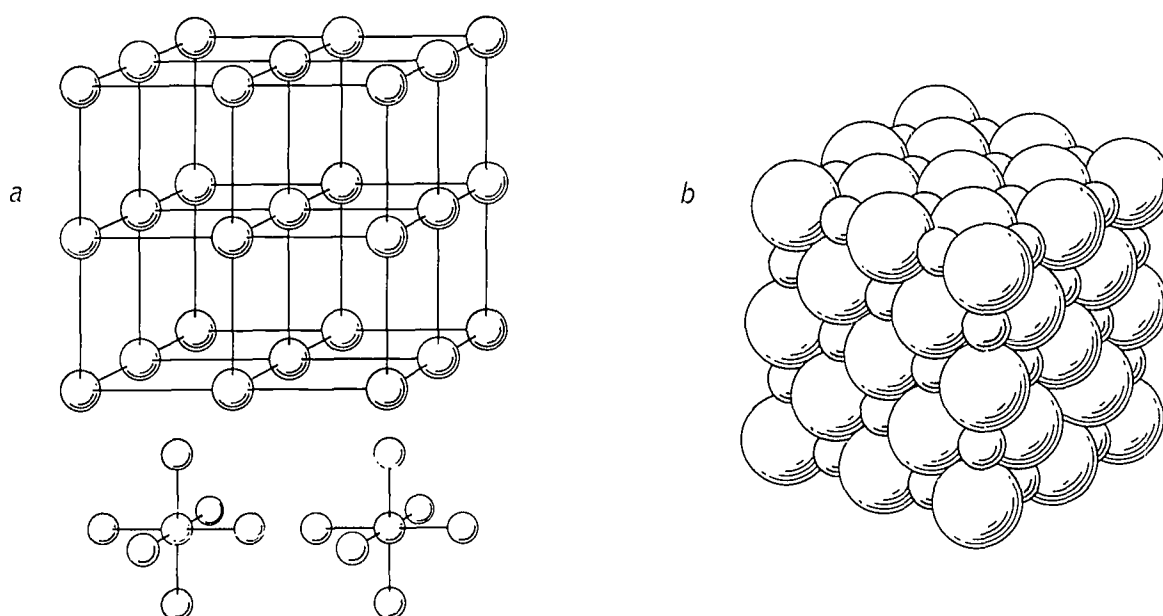
If, on the other hand, two simi-

5

Fig. 2.1   In solid sodium chloride, each negative ion is immediately surrounded by six positive ions, and each positive ion by six negative ions, as shown at the left. Diagrams of atomic arrangements in crystals usually show just the locations of the centers of the atoms, so that the arrangements can be seen more readily. The diagram at the right shows more truly how the ions pack together. It was drawn by William Barlow, who suggested more than seventy years ago that the atoms in sodium chloride might take this arrangement in the solid. Objections were raised then that the structure does not portray the atoms as associated in diatomic molecules. But studies of sodium chloride crystals by X-ray diffraction have since shown that Barlow was right. In the solid the molecules, not the structure, had to be discarded. His diagram also shows correctly that one species of ions is larger than the other.

lar atoms come close to each other, there is no reason to expect charge to flow permanently from one to the other, for the two atoms are indistinguishable in kind, and there is no evidence that it does. Nevertheless they do attract each other, and often that fact can be explained by supposing that electronic charges move back and forth between the two atoms. Then instantaneously each has a charge opposite to that of the other. Moreover, while the electrons are moving they are instantaneously between the two atoms, and there they provide a cloud of negative charge that attracts both the atoms because, having contributed the negative charges in the cloud, the atoms bear net positive charges.

When two similar atoms join in this way, the attraction between them is called a covalent bond. Their electronic charges bond them in both these ways, as Chapters 5, 6, and 7 analyze in more detail. The electrons try to decrease their total energy: the sum of their kinetic energy and their potential energy. Their potential energy is lower when they are close to one or the other of the positively charged nuclei. But their kinetic energy is lower if they can range over a wider space, because then their de Broglie wavelength λ is longer, and their momentum $p = h/\lambda$ is smaller.[4]

_____

[4] The connections between kinetic energy and the de Broglie wavelength, and the exclusion principle, are described in Wave-Mechanical Properties of Stationary States, a monograph in this series.

Hence there is a competition between the decrease of kinetic energy and the increase of potential energy of the electrons when they make wider excursions from the atoms. When two atoms permit an electron to visit them, and so to decrease the electrontronic kinetic energy, the electron may find that its total energy is lowered by visiting back and forth. In order to make such visiting worth while, each atom must offer to the electron a permitted state whose energy is low enough, and which is not already occupied by another electron. The latter qualification, coming from the exclusion principle, is the more stringent: more than any other single principle, it distinguishes the bonds that are possible from those that are not.[4]

Thus in a covalent bond two similar atoms are held together by electrons that exchange places between them. Part of the time that exchange gives the atoms opposite net charges, and the rest of the time it leaves both of them with a net positive charge that is attracted toward a concentration of negative charge between them, as Fig. 2.2 suggests. This is usually a localized phenomenon. The electrons participating in the bond are contributed by both of the bonded atoms, and commonly they extend their allegiance no further; the bond is localized between the two atoms. Each atom may be bonded to other atoms also, by other electrons. But each of these bonds can usually be pictured quite separately, engaging different electrons that do not move from one bond into another. In many cases the covalent bonding that links atom to atom comes to an end with relatively few atoms, to form a molecule; and then the bonding of molecule to molecule, to form a liquid or a solid, originates in forces whose character is not covalent. In diatomic molecules such as those composing hydrogen gas, there is only one covalent bond per molecule. In a molecule of the hydrocarbons of which paraffin
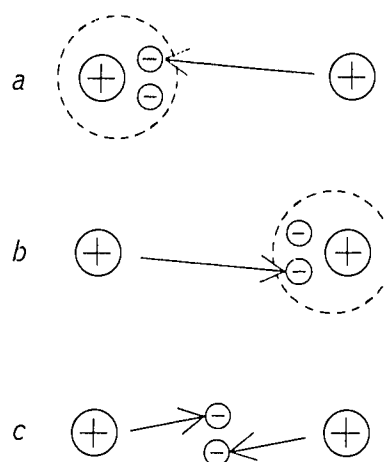
Fig. 2.2 Three formal arrangements of two electrons in a hydrogen molecule. When both electrons are near one or the other nucleus (a and b), there is a net negative charge within the dotted line, and the two atoms attract each other as two ions would. When the electrons are between the nuclei (c), they attract both nuclei toward them, and thus toward each other.

Fig. 2.3 In a diamond, each carbon atom is immediately surrounded by four others, held to it by strong covalent bonds directed toward the four corners of a regular tetrahedron. The resulting network of bonds makes a diamond crystal a single giant molecule, and the bonds' strength gives to a diamond its extreme hardness.

consists, from twenty to fifty carbon
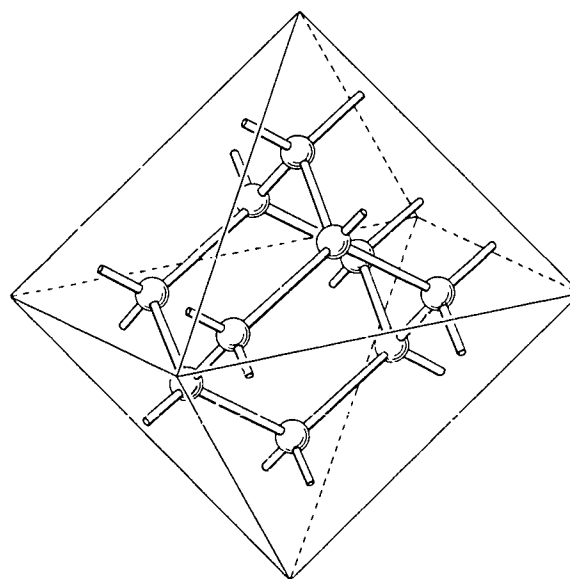atoms are covalently linked in chains,
and hydrogen atoms are covalently
bonded to them. The modern plastic,
polythene, consists of similar mole-
cules, but each contains many hundred
atoms linked together. Finally, in a
crystal of diamond, the constituent
carbon atoms are all joined by coval-
ent bonds as Fig. 2.3 shows into a
single gigantic molecule.
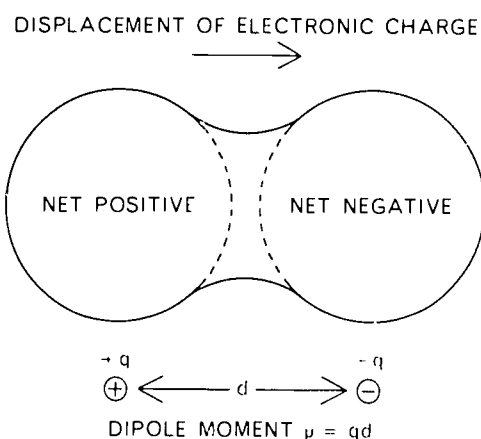
Notice, however, that since the

DISPLACEMENT OF ELECTRONIC CHARGE

NET POSITIVE | NET NEGATIVE

$+q$ $-q$

DIPOLE MOMENT $\mu = qd$

Fig. 2.4   If electronic charge is displaced
toward one of two bonded atoms, the pair
acquires a dipole moment.

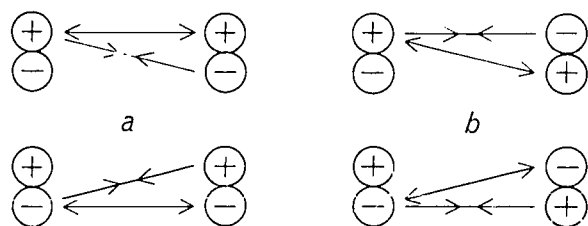a   b

Fig. 2.5   Two arrangements of two dipoles.
In arrangement a, the positive charge in
the dipole at left is slightly nearer to
the positive charge than to the negative
charge in the dipole at right, and hence
that charge repels the dipole slightly.
Similarly, the negative charge in the
dipole at left also repels the dipole at
right, and thus the two dipoles repel each
other. In arrangement b, the attractions
between the charges slightly outweigh the
repulsions, and the two dipoles attract
each other.

electrons participating in the bonding
of a molecule remain within the con-
fines of the molecule, they cannot
drift through the solid, and the solid
is an electrical insulator. Moreover
when the solid is heated it will usu-
ally melt into electrically neutral
molecules, not charged ions, and hence
the liquid will also be an insulator.
Yellow crystalline sulfur, for in-
stance, melts to a light-yellow in-
sulating liquid, each of whose mole-
cules contains eight sulfur atoms.

But there are exceptions to this
behavior, easily understood. When two
atoms of different species are bonded,
the bond may be changed from the
purely covalent toward the ionic. If
the energy of the state offered by one
atom is slightly lower than that of
the state offered by the other, the
average electronic charge will be dis-
placed toward the atom offering the
state of lower energy. When the mate-
rial is melted, the thermal agitation
may dissociate some of the molecules
into ions, and the melt may therefore
show ionic conduction of electricity.

The displacement of charge to-
ward one of the two bonded atoms gives
to the pair of atoms a dipole moment.
as Fig. 2.4 points out. Such dipole
moments within molecules are important
contributors to the bonds between the
molecules in a liquid or solid. The
force between two dipoles varies not
only with their separation but also
with their relative orientation, as
Fig. 2.5 shows. Since favorable rela-
tive orientations will afford lower
electrostatic energies than unfavor-
able orientations, the molecules will
tend to assemble into a favorable
arrangement, held together by dipole-
dipole forces. If the molecules are
large and contain several species of
atoms, the stray fields from the in-
dividual dipole moments of the several
bonds can add together to give a force
whose spacial dependence is quite com-
plicated, and the total force holding
one molecule to another can be quite
large. Partly for this reason, large
and complicated organic molecules

often form crystals that melt at moderately high temperatures.

Even when the bonds have no dipole moment, however, the molecules attract one another. The picture of the covalent bond formalized in Fig. 2.2 offers two reasons for this attraction. In the first place, the concentration of negative charge midway between two equal positive charges gives the bond a "quadrupole moment" (Fig. 2.6). Again favorable orientations permit an attraction between two quadrupoles, but that attraction is weaker and falls off more rapidly with distance than the attraction between two dipoles.

In the second place, the flow of charge back and forth between the two atoms, so that each is alternately positive and negative, gives the bond an oscillating dipole moment. If such oscillations are properly phased in neighboring molecules, the fluctuating dipole moments will make the molecules attract one another, much as do the fixed dipole moments in some of the arrangements of Fig. 2.5.

It turns out that this second sort of contribution will always be present, not only between molecules but also between atoms. The analysis carried out in Chapter 4 shows that the force increases with the <u>polarizability</u> of the molecules or atoms - the ratio of the dipole moment induced by an electric field to the magnitude of the inducing field. Since the polarizability of an atom or molecule increases in rough proportion to its volume, as the next chapter shows, these forces tend to be larger between larger molecules.

The temperature at which a material boils provides a rough qualitative measure of the forces between .'s molecules: in order to boil the material, enough energy must be supplied to it to separate its molecules. Table 2.1 shows how the properties of some organic substances support the preceding picture of how their molecules interact. The hydrocarbons, which have no dipole moment, boil at
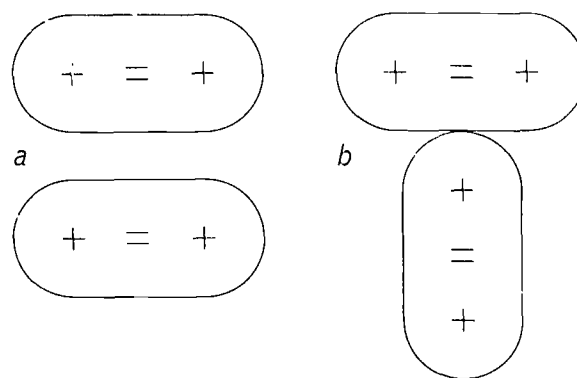

Fig. 2.6 Two arrangements of the quadrupoles in two covalently bonded molecules: (a) higher energy (less favorable), and (b) lower energy (more favorable).

much lower temperatures than the corresponding alcohols, which are polar. Furthermore, in both series of compounds, the boiling points increase as the size of the molecules increases.

There are still other electrostatic effects that will contribute to the bonding between molecules. If fixed ionic charges are present, they will tend to polarize neighboring atoms and molecules - to shift the centers of charge in them slightly so that they acquire dipole moments even if they had none in the absence of the ions, as Figure 2.7 (see next page) suggests. These dipole moments then exert forces on one another and on the ions responsible for them. Similarly, though less strongly, fixed dipole moments in some bonds will induce dipole moments elsewhere.

Collectively these electrostatic

HYDROCARBONS		ALCOHOLS	
METHANE (CH_4)	−161	METHYL (CH_3OH)	+ 67
ETHANE (C_2H_6)	−73	ETHYL (C_2H_5OH)	+ 78
PROPANE (C_3H_8)	−45	PROPYL (C_3H_7OH)	+ 97
BUTANE (C_4H_{10})	+1	BUTYL (C_4H_9OH)	+117

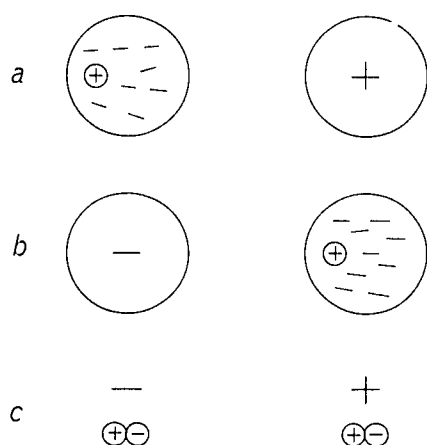Table 2.1 Boiling points in degrees centigrade.

Fig. 2.7 Two oppositely charged ions in-
duce dipoles in each other. The positive
ion attracts the negatively charged cloud
in the negative ion (a), and the negative
ion repels the negatively charged cloud in
the positive ion (b). The resulting dipoles
in the two ions are so arranged that they
contribute an additional attractive force
to the force between the ionic charges.

forces from so-called stray fields are
usually termed van der Waals forces,[5]
and are distinguished from strictly
ionic forces, as well as from covalent
bonding forces. The particular sort
of van der Waals force that is due to
the correlation in the phases of
oscillating dipoles is often disting-
uished as the dispersion force. The
distinction is useful because the
dispersion force stands somewhat apart
from other van der Waals forces in
three respects. In the first place it
is the only attractive force that
operates between isolated neutral
atoms - atoms that are not ionized or
covalently bonded. In the second place
it is independent of the relative
orientations of the participants (ex-
cept insofar as their polarizabilities
depend on direction) and it is addi-
tive. Each atom or molecule can be
thought to contain a host of oscillat-

ing dipoles, each properly phased to
interact attractively with an oscil-
lating dipole in each companion atom
or molecule. In the third place the
force is always present, even between
ions and between the inner electronic
cores of atoms that are covalently
bonded by their outer electrons.

But all the van der Waals forces
are significantly weaker than ionic
and covalent bonding forces. Moreover
they fall off more rapidly with dis-
tance. The force between two ions
separated by a distance r falls off
as $1/r^2$. Between two permanent dipoles,
with fixed relative orientations, the
force falls off as $1/r^4$; and between
two atoms interacting with the dis-
persion force, it falls off as $1/r^7$.
Their smaller magnitude and more rapid
disappearance with distance permit a
solid bonded by these forces to melt
at a lower temperature than ionically
and covalently bonded materials. The
melting point of solid argon, whose
crystals are made of closepacked
neutral atoms, is -190° C, whereas
potassium chloride, the ionic crystal
formed from the two elements with
atomic numbers one greater and one
less than argon, melts at $+776^{\circ}$C.

Return now to the picture of co-
valent bonding, and in particular to
the argument that an electron will re-
duce its kinetic energy by extending
its excursions as far as it can. Evi-
dently that argument will account for
the fact that the electrons in metals
roam throughout the material. The
roaming electrons provide a sea of neg-
ative charge in which swim the posi-
tive ions that have contributed those
electrons. The negatively charged sea
between the ions holds them together,
and the attraction of the ions in turn
prevents the sea from flowing away.

Then why are not all materials
metallic? Looking at the periodic
table, you will find that most of the
elements do solidify as metals, and
the solid metals melt into metallic
liquids. In nonmetallic materials the
roaming of the electrons would in-
crease their potential energy more

[5]The Dutch physical chemist, Johannes van der
Waals, was the first to take into account ex-
plicitly the effect of these attractive forces
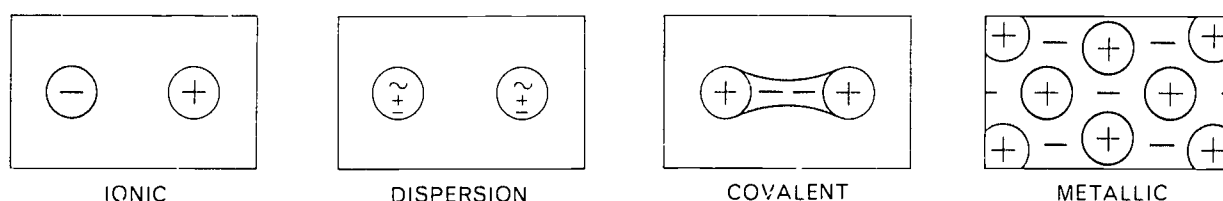on the properties of gases.

Fig. 2.8 Memory aids for the four extreme types of bonding.

than it would decrease their kinetic energy; it would require them to spend too much time too far from the positively charged nuclei.

Whenever the electrons can make those excursions, roaming from atom to atom indiscriminately to give the liquid or solid metallic properties, an electric field will make the electrons drift. The resulting "electronic" conduction is distinguishable from ionic conduction by the fact that the nuclei do not drift, and thus no products of electrolysis are deposited at the electrodes. In such a case, even in the liquid, the electrons can drift so much more readily than the nuclei and their surrounding cores of bond electrons that

the conductivity is still electronic.

There are some materials whose molecules give some of their electrons freedom to roam within the confines of a molecule, but not to roam from molecule to molecule. In a molecule of benzene, for example, six electrons are free to roam about a ring of six carbon atoms. But the electrons cannot escape from the molecule, and hence benzene is an electrical insulator.

In summary, it is conventional to distinguish four extreme types of bonds: (1) ionic bonds, forming "ionic" solids; (2) covalent bonds within molecules, or within complex ions such as SO_4, and sometimes linking together the atoms in an entire crystal to form solids such as diamond; (3) van der

SOLID TYPE	CRYSTAL UNITS	BINDING FORCE	OPTICAL	ELECTRICAL	THERMAL	MECHANICAL	EXAMPLES
IONIC	SIMPLE AND COMPLEX IONS	ELECTROSTATIC ATTRACTION OF OPPOSITELY CHARGED IONS	TRANSPARENT, OR COLORED BY CHARACTERISTIC ABSORPTION OF IONS	INSULATORS, FORMING CONDUCTING SOLUTIONS IN IONIZING SOLVENTS	FAIRLY HIGH MELTING, TO FORM IONS	HARDNESS INCREASES WITH IONIC CHARGE; BREAK BY CLEAVAGE	SODIUM CHLORIDE, CALCITE, AMMONIUM SULFATE
MOLECULAR	RARE GAS ATOMS; MOLECULES	DISPERSION AND MULTIPOLE FORCES	TRANSPARENT, AND LIKE ITS MOLTEN FORM	INSULATORS; DISSOLVE IN NONIONIZING SOLVENTS	FAIRLY LOW MELTING	SOFT AND PLASTICALLY DEFORMABLE	ARGON, PARAFFINS, CALOMEL
ADAMANTINE	GROUP IV ELEMENTS; III-V AND II-VI COMPOUNDS	COVALENT, SOMETIMES PARTLY IONIC	TRANSPARENT, HIGH REFRACTIVE INDEX; OR OPAQUE	SEMICONDUCTORS EXCEPT DIAMOND; INSOLUBLE	VERY HIGH MELTING	VERY HARD; BREAK BY CLEAVAGE	DIAMOND CARBORUNDUM ZINC BLENDE
METALLIC	POSITIVE IONS AND "FREE" ELECTRONS	ATTRACTION BETWEEN IONS AND ELECTRON "GAS"	OPAQUE AND REFLECTING	ELECTRONIC CONDUCTORS; SOLUBLE IN ACIDS TO FORM SALTS	MODERATELY HIGH MELTING; GOOD HEAT CONDUCTORS	TOUGH AND DUCTILE EXCEPT TUNGSTEN	COPPER IRON SODIUM

Table 2.2 Properties of the solid.

Waals forces, forming "molecular" sol-
ids from neutral atoms and molecules;
and (4) the "metallic" bonds charac-
teristic of metals. With the under-
standing that its pictures must be
interpreted in terms of the preceding
discussion, Fig. 2.8 offers aids for
remembering the distinctions between
these four extreme types of bonds.
But any such classification is neces-
sarily rough. Thus a covalent bond be-
tween two different species of atoms
always has some ionic character. By
polarizing its partner, an ion will
usually give to an ionic bond a partly
covalent character. The accumulation
of charge density along lines between
adjacent atoms in a metal will often
give the metallic bond a partly local-
ized property. The weak dispersion
force, hard to discern in the pres-
ence of stronger forces, is always
present. And the origin of all these
forces is ultimately the same: the
electrostatic attraction between posi-
tively charged atomic nuclei and nega-
tively charged electrons.

     Matter in the solid state exhib-
its especially clearly the distinc-
tions of the four classes of bonds out-
lined in this chapter. The form of
order adopted by the atoms when they

assemble into crystals is often diag-
nostic of many details in the charac-
ter of the interatomic bonding. Some
of the more conspicuous properties of
solids are suggested in Table 2.2,
which lists the four classes.

PROBLEMS

2.1 Why do many molecular crystals
    have low densities?

2.2 When a solid contains several
    sorts of bonds:

    (a) Would you expect its melting
    point to be determined ordinarily
    by its weakest bonds or its strong-
    est bonds?

    (b) Under what circumstances would
    you expect to find exceptions to
    your answers to (a)?

2.3 Discuss the quantitative change in
    bonding that accounts for the fact
    that the melting points of crys-
    tals of the halogens increase in
    the order $F_2 < Cl_2 < Br_2 < I_2$.

The dualistic theory of chemical combination proposed by Davy and Berzelius, although it is not as simply and widely applicable as they had hoped, explains quite successfully in a qualitative way the formation of chemical compounds by atomic species from opposite sides of the periodic table. At the turn of the century, even before Ernest Rutherford developed the picture of the planetary atom, J. J. Thomson had suggested that the electrons are arranged in groups or layers in an atom, and that the number of electrons in the outermost layer largely determines the chemical properties of the species.

According to Thomson, the atoms of the rare gases must contain especially stable arrangements of electrons. An atom with one electron less than a rare-gas atom - for example, chlorine - tends to acquire an extra electron and so to form a negative ion. An atom with one more electron - for example sodium - readily loses it, to form a positive ion. Atoms that readily lose electrons will combine chemically with atoms that tend to acquire electrons - a picture now familiar to all who have studied elementary chemistry.

It is interesting to examine some aspects of this theory in a more quantitative way. Consider, for example, the alkali halides - the compounds formed by the alkali metals Li, Na, K, Rb, and Cs, with the halogens F, Cl, Br, and I. The elementary picture portrays spherical ions having opposite charges of $+e$ and $-e$ (where e is the magnitude of the electronic charge, 4.8×10^{-10} electrostatic units) attracting each other electrostatically. It can be examined quite successfully without recourse to quantum mechanics, and by using a simple electrostatic argument it can be made to yield close quantitative agreement with experiment. But it needs some modification nevertheless, as this chapter will show.

In experimental fact, when a solid alkali halide is vaporized, the oppositely charged ions pair off into diatomic molecules, and the data obtained from the vapor can be used to verify the picture. For several such molecules, Table 3.1 shows the observed distances r_0 (in angstroms) between the centers of the ions, and the experimentally determined energy D (in electron volts) required to separate the ions by an infinite distance.[6] Electrostatic theory says that each spherically symmetric distribution of charge should behave toward charges outside it as if its total charge were concentrated at its center. Hence the picture predicts that $D = e^2/r_0$, and the last column of the table verifies the prediction.

Look now at the relationship between these measurements and some others that bear upon them. For example, measurements of the ionization energy of sodium show that 5.1 eV of energy is required to remove to an

[6]The units employed are described in the associated Discussion 3.1, Units. "Infinite" means here so far that they interact negligibly.

	r_0 (ANG-STROMS)	D (ELECTRON VOLTS)	Dr_0/e^2
KF	2.55	5.8	1.03
KCl	2.79	4.92	0.95
KBr	2.94	4.64	0.95
KI	3.23	4.51	1.01
NaCl	2.51	5.54	0.96
NaBr	2.64	5.33	0.98
NaI	2.90	5.14	1.09

Table 3.1   Molecules of alkali Halides.

Discussion 3.1

UNITS

By employing electrostatic units of electrical charge, and one centimeter as the unit of length, our formulas will yield energies in ergs, and electric fields in dynes per unit charge. For greater convenience in different physical and chemical contexts, different units of distance and of energy are often used, and it is helpful to become acquainted with some of them. The underline angstrom unit of length is widely used in quoting distances of atomic size.

1 angstrom (1 Å)

$= 10^{-8}$ centimeter $(10^{-8}$ cm$)$.

A unit of energy commonly used in speaking of the behavior of matter on an atomic scale is the electron volt – the kinetic energy acquired by an elec-tron accelerated through a potential difference of one volt.

1 electron volt (1 eV)

$= 1.6 \times 10^{-12}$ erg.

In speaking of bulk matter, on the other hand, chemists especially use as a unit of energy the kilogram-calorie per mole - the heat-equivalent of the energy, reckoned for Avogadro's number (6.03×10^{23}) of molecules.

1 kilogram-calorie (1 kcal)

$= 4.18 \times 10^{10}$ ergs.

It is convenient to bear in mind the approximate conversion factor

1 eV per particle

$= 23$ kcal per mole of particles.

infinite distance one electron from each atom of sodium. Measurements of the electron affinity of chlorine show that 3.7 eV of energy is returned when one electron is returned from an infinite distance to an atom of chlorine. At first glance, passing one electron from a sodium atom to a chlorine atom may seem unfavorable, to the extent of 1.4 eV per molecule of sodium chloride.

You are rescued by noticing that, if the sodium chloride molecule were formed in this way, the two ions would still be separated by a great distance. For the purpose of quantitative argument the formation of the ionic bond in sodium chloride could be imagined to occur in the three stages shown in Fig. 3.1. In the approach of the two ions to their final separation (stage 3) there can be a gain of energy more than compensating the net loss in the first two stages. The energy in stage 3 is clearly the dissociation energy in Table 3.1.

Now examine some simple modifications that must be introduced into the preceding model of the ionic bond. For example, the calculation summarized in Table 3.1 assumes that the atoms are infinitely hard, incompressible balls, attracting each other until they bump. Of course their structure is not really as rigid as that: all matter, even solid matter, is compressible. Fig. 3.2 diagrams the difference between the picture lying behind the calculation and the picture suggested by the compressibility of atoms. The attraction between the oppositely charged ions pulls them together until
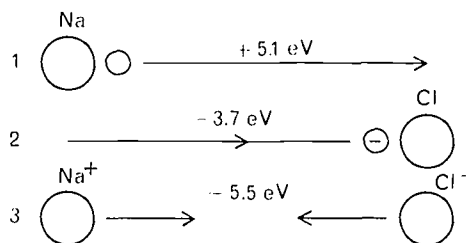

Fig. 3.1   The bond between sodium and chlorine is almost purely ionic because the dissociation energy (3) is so much greater than the difference between the ionization potential (1) of sodium and the electron affinity (2) of chlorine. The energies are given in electron volts.

Discussion 3.2

EQUILIBRIUM SEPARATION OF IONS

The energy of interaction of two ions, at any separation r, is well represented by the expression

$$E = -e^2/r + B/r^n.$$

The equilibrium separation r_0 is attained when E reaches a minimum. This fact enables the constant B to be determined in terms of r_0 as follows. The derivative of E with respect to r is

$$\frac{dE}{dr} = \frac{e^2}{r^2} - \frac{nB}{r^{n+1}}.$$

Setting that derivative equal to zero at $r = r_0$ gives

$$\frac{nB}{r_0^{n+1}} = \frac{e^2}{r_0^2}, \text{ or } B = \frac{e^2 r_0^{n-1}}{n}.$$

The energy E when $r = r_0$ is the dissociation energy of the molecule:

$$D = \frac{-e^2}{r_0} + \frac{B}{r_0^n}.$$

Using the value of B just found,

$$D = \frac{-e^2}{r_0} \left(1 - \frac{1}{n}\right).$$

In other words, at the equilibrium separation, the repulsive energy is equal to the n'th part of the attractive energy.

the repulsive force between them balances the attractive force, and the energy of their interaction is a minimum.

The origins of this repulsive force lie in the properties of electrons that are summarized in the exclusion principle. As the two ions approach each other, the electrons in each are more and more required to occupy space already inhabited by the electrons in its partner. In order to do so, they must find states in that space. But the states permitted to a
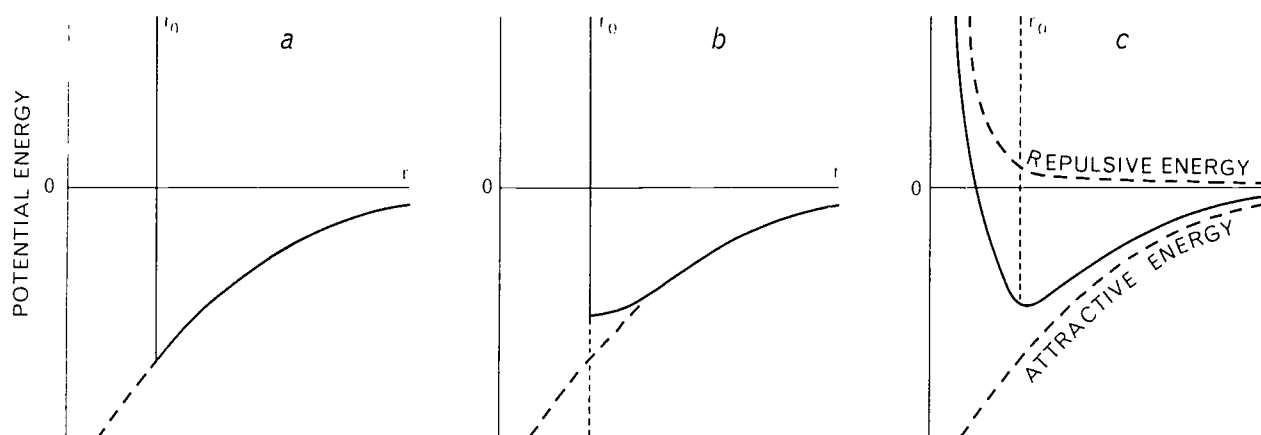

Fig. 3.2 The assumption that two oppositely charged ions are hard spheres, attracting each other until they bump, yields the energy diagram (a). But in fact the ions feel a repulsive force, which increases rapidly as they approach each other (b). The truth is better represented (c) as the sum of a repulsive energy and an attractive energy, which reaches a minimum at the actual separation of the ions.
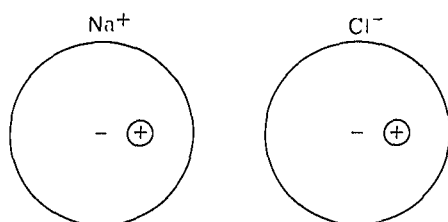
Fig. 3.3 The net charge on each ion polar-
izes the other ion, and the resulting
dipoles are so oriented that they attract
each other.

bound electron are discrete and defi-
nite, each with a definite energy;
and only two electrons, with their
spins opposed, can occupy any one of
them. Thus the electrons in the ap-
proaching ions are forced into states
whose energies increase rapidly as the
distance between the ions decreases.

Look now for a way to take this
repulsive interaction into quantita-
tive account. Although no theory so
simple as that of the electrostatic
attraction is available to guide you
in studying the repulsion, you can re-
sort to a device that is often em-
ployed in similar situations. Choose
a mathematical expression that has a
general behavior suitable for repre-
senting a repulsive force, and that
affords enough adjustability to accom-
modate some variation from one mole-
cule to another.

In this case it is suitable to
add to the attractive potential energy,
$-e^2/r$, a repulsive potential energy,
B/r^n, where r, the distance between
the ions, is allowed to vary. The un-
determined coefficient B and exponent
n confer the desired adjustability:
the former measures the strength of
the repulsion and the latter measures
the sharpness with which the repulsive
force increases as the ions approach
each other. The energy of the pair of
ions at any separation, relative to
that of the infinitely separated ions,
then becomes

$$E = -e^2/r + B/r^n. \qquad (3.1)$$

In order to make comparisons of
this expression with experiment, the
two constants B and n must be deter-
mined by resort to two properties of
the pair of ions, independently meas-
ured or calculated. One property avail-
able for this purpose is the experi-
mental interatomic separation r_0
listed in Table 3.1. Since E must
reach a minimum when $r = r_0$, B can be
put in terms of r_0 in the way shown
in Discussion 3.2. Equation (3.1) then
yields an expected dissociation en-
ergy at the actual separation r_0

$$D = \frac{e^2}{r_0} \left(1 - \frac{1}{n}\right). \qquad (3.2)$$

Discussion 3.3

DIPOLE MOMENTS

The dipole moment of the charges
+q and −q, separated by a distance d,
is defined as $\mu = qd$. Evidently in a
fixed coordinate system whose x axis
lies along the line determined by the
locations x_1 and x_2 of the two charges,
the preceding definition is equivalent
to the expression $\mu = q(x_1 - x_2)$, or

$$\mu = q_1 x_1 + q_2 x_2$$
where
$$q_1 = -q_2 = q.$$

When there are many charges, of
different magnitudes and signs, q_1,
q_2 . . . whose positions are $(x_1, y_1,
z_1)$, (x_2, y_2, z_2), . . . the dipole
moment of the collection can be de-
fined in an analogous way as a vector
whose components are

$$\mu_x = q_1 x_1 + q_2 x_2 + \cdots$$
$$\mu_y = q_1 y_1 + q_2 y_2 + \cdots$$
$$\mu_z = q_1 z_1 + q_2 z_2 + \cdots$$

Clearly the repulsive energy, by reducing the expected dissociation energy, will damage the agreement with experiment shown in Table 3.1, by an amount depending on the value of n. Suitable values of n have been found by examining the compressibilities of crystalline alkali halides; they lie between 8 and 10. Hence the calculated values of D will now be smaller than the experimental values by about ten per cent.

Fortunately there is a second important modification of our model of ionic bonding that will increase the calculated attractive energy, and so tend to compensate the repulsive energy. As the preceding chapter pointed out, each ion will polarize its partner, and the dipole moments so induced will be favorably oriented to provide an additional attractive force between them (Fig. 3.3).

In order to find the size of this effect, it is necessary to examine first the polarizability of atoms and ions. The polarizability α of an atom, an important quantity in many calculations, is the magnitude of the dipole moment μ that an electric field $\vec{E}$ will induce in an atom per unit electric field:

$$\mu = \alpha\vec{E}. \qquad (3.3)$$

The dipole moment of a pair of equal and opposite charges is defined in turn as the product of the separation of the charges by the magnitude of the charge on either, and the definition can be extended, as in Discussion 3.3, to apply to a collection of any number of charges.

The picture to hold in mind while using Eq. (3.3) in the present case is that suggested in Fig. 3.4. The atomic model consists of a nucleus with a charge +Ze (where Z is the atomic number of the atom) which is embedded in a spherically symmetrical cloud of negative charge totaling −Ze contributed by the electrons. When the atom is undisturbed, the nucleus is at the center of the electronic cloud and

the atom has no dipole moment. When an electric field $\vec{E}$ is applied to the atom, the nucleus shifts within the cloud a distance a from its center.

To answer the question of how large a dipole moment that shift produces is difficult if we try to take into account how the density of charge within the electron cloud varies as one proceeds through it. But to make a rough calculation, sufficient for this purpose and many others, a greatly simplified model of the electronic cloud will avail. Take the charge −Ze as uniformly distributed within a sphere of radius R.

Then you can reason as follows. The force exerted on the nucleus by the field is $Ze\vec{E}$. That force will
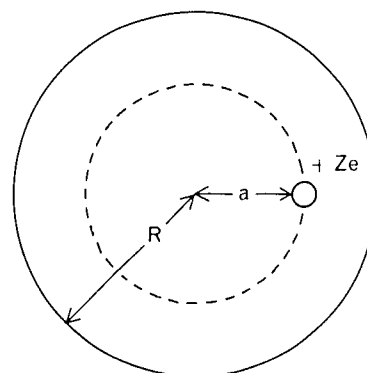

Fig. 3.4 To estimate the polarizability of an atom, approximate its structure by a uniform cloud of negative charge of radius R surrounding the positively charged nucleus.

ION	$\alpha^{1/3}$ (ANGSTROMS)	RADIUS (ANGSTROMS)
Na$^+$	0.91	0.97
K$^+$	1.10	1.33
Mg^{++}	0.87	0.66
Ca^{++}	1.05	0.99
F$^-$	1.02	1.36
Cl$^-$	1.21	1.81
O$^-$	1.11	1.40
S$^-$	1.29	1.84

Table 3.2 Polarizabilities of ions.

shift the nucleus until it is bal-
anced by a restoring force, which can
be taken as ka, a force proportional to
the displacement a, where k is some
force constant, soon to be estimated.[7]
But the dipole moment of the atom is
now $\mu = Zea = \alpha\vec{E}$. When the displace-
ment a is eliminated between this
equation and the equation $Ze\vec{E} = ka$,
the polarizability is given in terms
of the force constant by

$$\alpha = \frac{(Ze)^2}{k}. \qquad (3.4)$$

In order to estimate the magni-
tude of the force constant, assume
that the restoring force on the nu-
cleus is simply the electrostatic
force exerted on it by the charge
cloud, which tries to move the nucleus
back to the center. It is a familiar
result of electrostatic theory that a
charge that is wholly inside a spheri-
cal shell of charge experiences no
force from the shell. Hence the elec-
trostatic restoring force is exerted
by the fraction of the negative charge
that is nearer to the center than a,
or in other words the charge $-Zea^3/R^3$.
And that charge acts as if it were
concentrated at the center, according
to the electrostatic result used al-
ready at the beginning of this chapter.

Coulomb's law may now be used to
calculate the restoring force on the
nuclear charge +Ze: the force has the
magnitude ka = (Ze) · (Zea^3/R^3)
· $(1/a^2)$. Hence k = $(Ze)^2/R^3$, and a
comparison of this expression with
Eq. (3.4) yields the simple relation

$$\alpha = R^3. \qquad (3.5)$$

It is worthwhile to notice that the
equation gives to the polarizability
the dimensions of volume; and this is
in fact the correct dimensionality

(Problem 3.1), whether or not the
equation is accurate.

In order to decide how accurate
it is, experimentally measured polar-
izabilities can be compared with ex-
perimentally measured sizes of ions.
The polarizabilities are obtainable
from interpretations of optical exper-
iments; the sizes are obtainable from
observations of how the ions pack to-
gether in crystals. As Table 3.2
shows, the rough calculation of polar-
izabilities turns out to be quite
good. The measured polarizabilities of
the listed ions increase roughly with
the ionic volumes, but a little more
slowly. Hence the agreement is better
for small ions than for large.

These results can now be used to
estimate the contribution made by
polarization to the attractive energy
in the ionic bond. Since the radii of
the ions are of the order 1 Å = 10^{-8}
cm, the polarizabilities are of the
order 10^{-24} cc. An ion with one elec-
tronic charge (of magnitude
e = 4.8×10^{-10} esu) establishes an
electric field at a distance 2.5 Å
(the typical interionic separation
shown in Table 3.1) of the order
$\vec{E} = e/r_0^2 \doteq 10^6$ esu. Hence each ion in-
duces in its partner a dipole (Fig.
3.3) whose moment is of the order
$\mu = \alpha\vec{E} \doteq 10^6 \times 10^{-24} = 10^{-18}$ esu.[8]

As Discussion 3.4 shows, two di-
poles in the orientation shown in
Fig. 3.3 have an interaction energy
$-2\mu^2/r^3$. Substituting the magnitude of
the dipole moment just calculated,
and a typical value of r from Table
3.1, yields an interaction energy of
about 0.13 eV. Thus the inclusion of
polarization energy can remove some of

---

[7] The assumption of proportionality - of "linear-
ity" - is one of the most important and widely
applicable of simplifying assumptions used in
calculating the properties of physical models.

[8] This order of magnitude is characteristic of
atomic and molecular dipole moments - not only
those induced by applied fields but also those
permanently resident in molecules, described in
the last chapter. For this reason 10^{-18} esu is
often taken as a unit in the quantitative dis-
cussion of molecular dipoles. So taken, it is
called the "Debye unit," after Peter Debye who
developed a classic theory of the behavior of
molecular dipoles.

Discussion 3.4

DIPOLE-DIPOLE INTERACTION

In order to find the attractive energy of two dipoles that point in the same sense along their own direction, add the electrostatic energies of interaction of all the charge pairs within the dipoles:
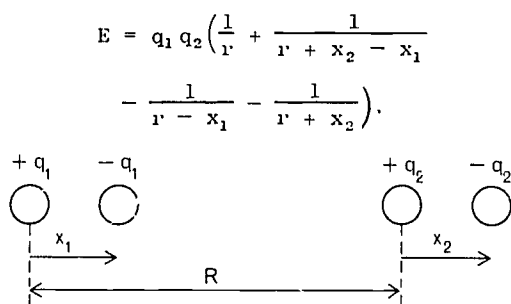
$$E = q_1 q_2 \left(\frac{1}{r} + \frac{1}{r + x_2 - x_1} - \frac{1}{r - x_1} - \frac{1}{r + x_2} \right).$$

Expand each fraction in series, taking x_1 and x_2 small compared with r, and retaining only the first significant term in small quantities:

$$E = \frac{q_1 q_2}{r} \begin{bmatrix} 1 \\ +1 - \dfrac{x_2 - x_1}{r} + \dfrac{(x_2 - x_1)^2}{r^2} - \cdots \\ -1 - \dfrac{x_1}{r} - \dfrac{x_1{}^2}{r^2} - \cdots \\ -1 + \dfrac{x_2}{r} - \dfrac{x_2{}^2}{r^2} + \cdots \end{bmatrix}$$

Thus $E \doteq -2(q_1 x_1)(q_2 x_2)/r^3 = -2\mu_1 \mu_2/r^3$.

the damage that the inclusion of repulsive energy worked on the agreement in Table 3.1. A third important consideration in comparing these calculations with experimental results is suggested in Problem 3.3.

The foregoing discussion of their compressibility and distortability suggests that ions appear to be rigid only because the forces ordinarily encountered in our world are too feeble to affect them much. For many practical purposes the rigid-sphere model of an ion is remarkably useful. For example, ascribing to ions effective radii, which depend mostly on their species and little on their environment, proves to be a valuable guide in understanding the choice of crystal structure adopted by a large collection of oppositely charged ions.

PROBLEMS

3.1 Check the fact that polarizability has the dimensions of volume by proceeding directly from Eq. (3.3), which defines that quantity. For this purpose notice (1) that a dipole moment has the dimensions of charge times distance, (2) that an electric field has the dimensions of force per unit charge, and (3) that Coulomb's law so defines the dimensions of charge that force must have the dimensions of charge-

squared divided by distance-squared.

3.2 Thermal agitation causes an alkali halide molecule to vibrate about its equilibrium length r_0. Since it is then an oscillating dipole, it can interact with electromagnetic radiation. Use Eq. (3.1) and the results of Discussion 3.2 to calculate the vibration frequency of the sodium chloride molecule.

In what range of the electromag-
netic spectrum does this frequency
lie?

3.3 Quantum mechanics has shown that
any harmonic oscillator retains a
minimum vibrational energy $\frac{1}{2}h\nu$,
where ν is its frequency and h is
is Planck's constant (6.62×10^{-27}
erg sec). Hence, even when it is
not thermally excited, an alkali
halide molecule must have an en-

ergy higher (less negative) than
the energies calculated in this
chapter, by the amount of this
so-called "zero-point energy."
Calculate the magnitude of that
zero-point energy, using the fre-
quency calculated in Problem 3.2.
By taking it into account, do you
better or worsen the agreement of
the calculated with the experi-
mental dissociation energy?

The rare gases such as neon and argon are remarkably inert: they do not form ionic bonds, and they show little tendency to share electrons with other atoms to form covalent bonds. Hence at first glance one might expect to find no attractive force between the atoms, but only a repulsive force when they come close to one another. As a matter of experimental fact, however, the atoms do attract one another weakly when they are near together, though still far enough apart so that repulsive forces do not dominate the interaction.

In order to understand these weak forces, it is well to remember that the electrons are not actually stationary charge clouds around the nuclei but rapidly moving swarms of negatively charged particles. On the average the center of gravity, and therefore the center of charge, of the electrons is at the position of the nucleus about which they swarm; but instantaneously it is not, and the atom has a rapidly fluctuating dipole moment. It might seem at first that this cannot lead to attraction

between the two atoms because the average dipole moment of each is zero. But if the oscillations of the dipole moments of the two atoms are correlated in phase, an attractive force can arise, as Fig. 4.1 suggests.

That figure portrays the instantaneous dipole moments of two neighboring atoms, varying with time and perfectly correlated in phase, so that they attract each other maximally at all times. A glance at Discussion 2.4 makes clear that in that case the energy of the system would be lowered by the amount $2\mu_1\mu_2/r^3$ averaged over time. It is tempting to argue that, since a system tries to readjust itself into a condition of minimum energy, the correlation will be perfect. But the electrons are subjected within the atoms to other influences, and some are much stronger than this weak interaction between the two atoms.

Then how closely can these oscillating dipoles correlate their phases? There are several ways of answering this question, all of which give results that are at least qualitatively consistent.
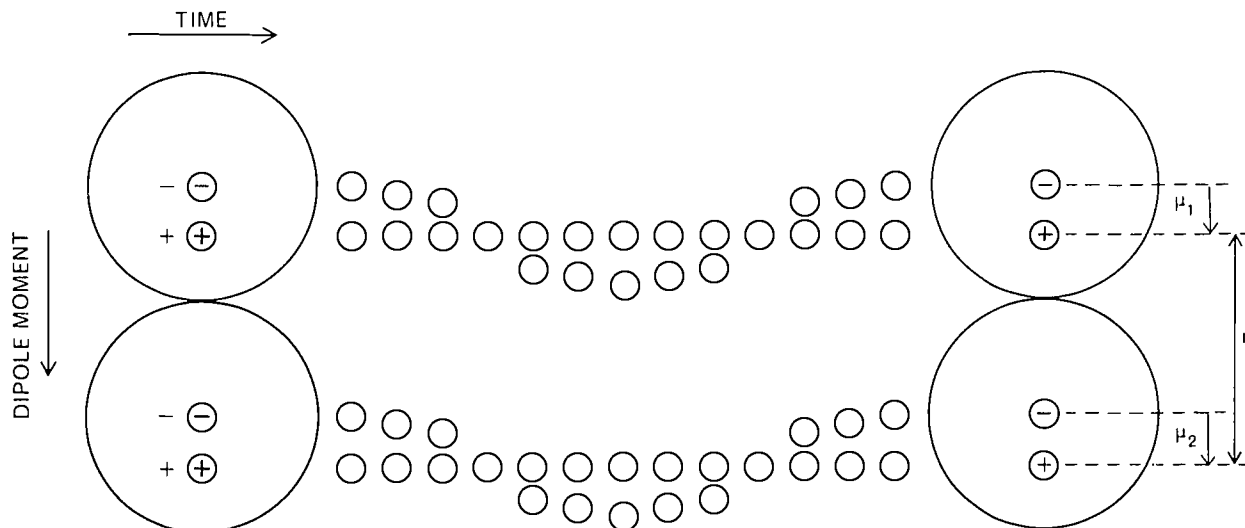

Fig. 4.1 A pair of dipoles, oscillating in phase in two atoms, could attract each other at all times. But the dipoles in adjacent atoms are not so closely correlated.
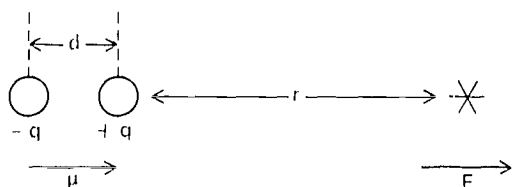
21

Fig. 4.2 The electric field due to a
dipole, at a distance r along its direction,
is the field due to the two charges that
form the dipole. By a procedure like that
of Discussion 3.4, $\overline{E} = q\left[1/r^2 - 1/(r+d)^2\right]$
$+ 2\ qd/r^3 = 2\ \mu/r^3$. Notice that, by conven-
tion, the vector representing a dipole mo-
ment points from its negative toward its
positive charge.

The simplest way is to think of
the fluctuating dipole in one atom as
establishing a fluctuating electric
field at the second atom. Then, using
the results of the discussion of polar-
izability in the last chapter, one can
conclude that the magnitude of the
correlated dipole in the second atom
will be the product of the polarizabil-
ity of the second atom times the elec-
tric field due to the dipole in the
first atom.

To pursue this calculation, no-
tice that the field due to a dipole
of moment μ_1, at a distance r, is
$2\mu_1/r^3$ (Fig. 4.2). If the polarizabil-
ity of the second atom is α, the in-
duced dipole has a moment given by
$\mu_2 = 2\alpha\mu_1/r^3$. Hence the potential en-

ergy of the combination of the induced
dipole and the original dipole is
$-2\mu_1\mu_2/r^3 = -4\alpha\mu_1{}^2/r^6$. Although μ_1 is
fluctuating, and its average value is
zero, $\mu_1{}^2$ is positive: the value of
$\mu_1{}^2$ averaged over time is the rele-
vant quantity to use in this expres-
sion for the potential energy.

Two results of this simple analy-
sis are important. In the first place,
the potential energy function for this
interaction varies as $1/r^6$. It falls
off very rapidly as the distance be-
tween the atoms increases; the force,
falling off as $1/r^7$,[9] is a short-
range force in contrast with the at-
traction between two ions, which falls
off as $1/r^2$. In the second place, the
force is larger the larger the polar-
izability of the atom.

But it is hard to find any method
for calculating the average value of
$\mu_1{}^2$, and so to find the order of mag-
nitude of the force. For this reason,
and in order to improve confidence in
the quantitative relations that the
model proposes between this force and
the polarizability and interatomic
separation, it is useful to look at
an alternative method of handling the
problem.

In the second method the fluctu-
ating dipoles of the two atoms are
treated as a pair of oscillators that
are weakly coupled by their interac-
tion. The method is more satisfying in
two respects. It deals with the two
atoms on the same footing at the out-
set, instead of focusing attention on
one of them. Furthermore it leads
more naturally to the interpretation
of its results in terms of measurable
properties of the atoms.

Imagine two atoms that are iden-
tical, and that possess oscillating
dipoles in each of which the center of
positive charge stays fixed. The cen-
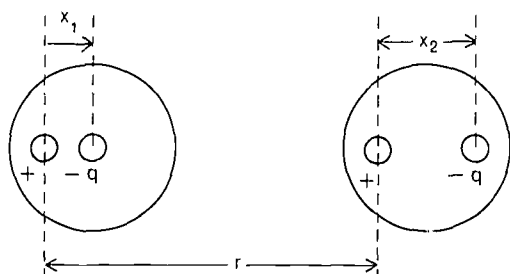ter of negative charge oscillates back

Fig. 4.3 In the coupled-oscillator model of
two atoms interacting with the dispersion
force, a portion of the negative charge
cloud in each atom is instantaneously dis-
placed from the nucleus, to give the atoms
instantaneous dipole moments of magnitudes
qx_1 and qx_2.

[9]Recall that the force, tending to increase the
value of a coordinate in a mechanical system,
varies as the negative of the derivative of the
potential energy of the system with respect to
the coordinate.

and forth along the line joining the positive charges so that the instantaneous displacements of each from the centers of positive charge are such as those denoted by x_1 and x_2 in Fig. 4.3. As in the study of polarizability in the last chapter, there is a force, proportional to the displacement, tending to restore the cloud of negative charge in each atom to the zero position; and again the force constant k can be related to the polarizability α of the atom.

Now simplify the picture of the fluctuating dipole moment of each atom into a simple harmonic oscillator with the force constant k whose mass m is the mass of the moving cloud of electrons. The natural frequency of the oscillator in each of the atoms is then

$$\nu_0 = \frac{1}{2\pi} \sqrt{\frac{k}{m}}. \qquad (4.1)$$

But when the atoms approach each other, the electrostatic interactions between the dipoles provide a weak coupling between them. The dipoles then behave like all other coupled oscillators: the coupling endows them with two distinct normal modes of vibration whose frequencies differ from ν_0 by amounts that increase as the coupling increases. In this case one frequency is higher and the other is lower than ν_0.

Assuming that each oscillator is in its ground state before it is coupled, you can take the energy of the uncoupled system as $2(\frac{1}{2}h\nu_0)$. Then when the system is coupled, its energy can be taken as $\frac{1}{2}h\nu_1 + \frac{1}{2}h\nu_2$, where ν_1 and ν_2 are the frequencies associated with the two normal modes of vibration. Since the average value of ν_1 and ν_2 is slightly lower than ν_0, the energy of the system is lowered by the coupling.

The details of the suggested calculation are shown in an appendix to this chapter. It leads to a calculated frequency

$$\nu_0 = \frac{q}{2\pi} \sqrt{\frac{1}{m\alpha}}, \qquad (4.2)$$

and a binding energy

$$\Delta E = \frac{3hq}{8\pi r^6} \sqrt{\frac{\alpha^3}{m}}, \qquad (4.3)$$

where h is Planck's constant, and q and m are the charge and mass of the oscillating charge-cloud.

It remains to decide what are reasonable values of q and m to use in this expression - what charge moves in the oscillator and what mass is associated with that charge. The calculated energy turns out to agree best with the observed energy when one assumes that only those electrons in the atom that are least tightly bound to the nucleus - those in the outermost shell - will readily suffer distortion of their states, and thus will make the major contributions to the oscillation. If there are N electrons in the outermost shell, $q = Ne_0$ and $m = Nm_0$, where e_0 and m_0 are the charge and mass of the electron. Then Eq. (4.3) can be written

$$\Delta E = \frac{3he_0}{8\pi r^6} \sqrt{\frac{N\alpha^3}{m_0}}. \qquad (4.4)$$

For convenience in practical calculation, it is helpful to rewrite this equation by making use of the facts that an atomic polarizability is of the order $10^{-24} cm^3$, and an interatomic distance is of the order $10^{-8} cm$. Expressing r' and α' in these units, the equation becomes

$$\Delta E = \frac{2.5 \times 10^{-11}}{(r')^6} \sqrt{N(\alpha')^3} \text{ ergs}.$$

Now check this result by calculating the binding energy of solid argon, and comparing the calculated value with that determined by experiments in which the heat required to vaporize argon is measured. Such a calculation proceeds by finding first the energy in a single bond between two argon atoms, and then multiplying that energy by the number of bonds in the solid. Since the dispersion force falls off so rapidly with increasing distance, only the bonds between the nearest neighbors need be considered.

In solid argon the distance between nearest neighbors is 3.84 Å.

The polarizability of an argon atom
is 1.66×10^{-24} cm^3, and there are
eight electrons in its outer shell.
With N = 8, and α' = 1.66, and
r' = 3.84, the equation yields
$\Delta E = 4.76 \times 10^{-14}$ erg, or 0.03 eV. It
is interesting to notice that the
ionic bond in a molecule of an alkali
halide, if the ions were separated by
the same distance, would have approxi-
mately the bonding energy e_0^2/r = 3.7
eV - more than a hundred times larger.

Argon crystallizes in a close-
packed structure (Fig. 4.4) giving
each atom twelve nearest neighbors at
the same distance. Since each nearest-
neighbor bond is shared between two
atoms, e number of bonds per atom
in the solid is six. Thus the binding
energy per atom of the solid is six
times the energy per bond. The calcu-
lated energy, 0.18 eV, is twice as
large as the experimental value,
0.09 eV.

In order to repair this dis-
crepancy between theory and experiment,
recall that our calculation has still
left out the repulsive energy - the
energy due to the repulsive force that
balances the attractive force between
the atoms and holds them at a fixed
distance. The preceding chapter showed
that the repulsive energy reduces the
calculated binding energy in the ionic
bond of an alkali halide molecule by
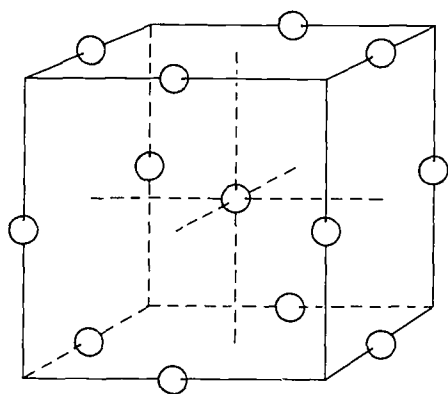about ten per cent. In the ionic bond

Fig. 4.4 In solid argon each atom is sur-
rounded by twelve others at the same dis-
tance.

the attractive force has a long range,
whereas the repulsive force has a
short range. But in the present case
the two forces that balance each other
are both of short range, and it be-
comes even more important to include
the energies due to both, as Problem
4.4 suggests.

Another way to obtain an approxi-
mate relationship between the disper-
sion force and other properties of an
atom is to relate the frequency ν_0 of
the oscillating dipole to some quan-
tity that can be determined experiment-
ally. The following crude argument,
for example, makes it seem reasonable
to relate that frequency to the first
ionization energy of the atom.

If the atomic dipole behaved in
a classical fashion, it could be
driven by an applied electromagnetic
force. If the applied force oscillated
with the frequency of the oscillating
dipole, the dipole would resonate. If
it resonated strongly, the amplitude
of its oscillation might increase suf-
ficiently to shake an electron out of
the atom.

Now in fact light can ionize
atoms, if each photon of the light has
sufficient energy to contribute the
ionization energy. Each photon of
light whose frequency is ν carries the
energy hν, where h is Planck's con-
stant. These facts suggest that the
ionization energy I of an atom be set
equal to hν_0, where ν_0 is the fre-
quency of its oscillating dipole.

By substituting I for hν_0 in the
equation $\Delta E = 3h\nu_0\alpha^2/4r^6$, derived in
the appendix, one obtains

$$\Delta E = \frac{3}{4} \frac{\alpha^2}{r^6} I. \qquad (4.5)$$

It turns out that binding energies
calculated from this equation agree
quite well with experimental values,
not only for atoms but for neutral
molecules that have no fixed dipole
moments, such as nitrogen and methane.
Table 4.1 shows the relevant quanti-
ties for several solid substances.
These successes give confidence in
calculating the contributions of dis-

	IONIZATION ENERGY (ELECTRON VOLTS)	POLARIZABILITY (cm³ x 10²⁴)	BINDING ENERGY (ELECTRON VOLTS PER MOLECULE)	
			CALCULATED	OBSERVED
Ne	21.5	0.40	0.017	0.026
A	15.7	1.66	⌐078	0.088
Kr	14.0	2.54	0.135	0.122
N₂	15.8	1.74	0.070	0.081
O₂	11.2	1.57	0.064	0.090
Cl₂	18.2	4.60	0.312	0.323
CH₄	14.5	2.58	0.107	0.117

Table 4.1   Binding Energies of Neutral Molecules

	DIPOLE MOMENT (ELECTROSTATIC UNITS x 10¹⁸)	POLARIZABILITY (cm³ x 1Ü	BINDING ENERGY (ELECTRON VOLTS PER MOLECULE)	
			CALCULATED	OBSERVED
HCl	1.07	2.63	0.176	0.220
HBr	0.78	3.58	0.197	0.240
HI	0.38	5.39	0.291	0.270

Table 4.2   Binding Energies of Hydrogen Halides

persion forces to the binding energies of materials in which the principal binding forces have other origins.

Calculation of energies due to dispersion forces explains also the binding energies of the solid hydrogen halides, shown in Table 4.2. The molecules of HCl, HBr, and HI have permanent dipoles, and their dipole moments decrease in that order. If the binding forces in crystals of these compounds came primarily from the interaction of the permanent dipole moments, the binding energies should decrease also in that order, whereas in fact they increase.

But other evidence has shown that, above certain critical temperatures characteristic for each compound, the molecules in these solids are rotating rapidly end for end. Time-average interaction of their permanent dipole moments can be no larger than the correlation of these rotations permits. As the temperature increases, that correlation decreases; it is negligible at their vaporization temperatures. Their heats of vaporization depend on the energies due to dispersion forces, which have the proper sequence to explain the observations on these materials.

Appendix   A COUPLED OSCILLATOR MODEL FOR THE DISPERSION FORCE

A harmonic oscillator of force constant k and mass m has potential energy $\frac{1}{2}kx^2$ and kinetic energy $p^2/2m$, where x and p are its instantaneous displacement and momentum, and it oscillates with a frequency $\nu_0 = 1/2\pi\sqrt{k/m}$. Thus the kinetic energy of the system of Fig. 4.1 is

$$U_{kin} = \frac{1}{2m}(p_1{}^2 + p_2{}^2) \qquad (A4.1)$$

and the potential energy is

$$U_{pot} = \tfrac{1}{2}kx_1{}^2 + \tfrac{1}{2}kx_2{}^2 - 2\frac{q^2 x_1 x_2}{r^3} \quad (A4.2)$$

where the last term is the instantaneous energy of their coupling as Fig. 4.1 describes.

The study of this system is facilitated by an elementary application of the method of normal coordinates.[10] In this case the normal coordinates x_1' and x_2' are given by

$$x_1 = \frac{1}{\sqrt{2}}(x_1' + x_2'), \text{ whence}$$

$$p_1 = \frac{1}{\sqrt{2}}(p_1' + p_2') \quad (A4.3)$$

$$x_2 = \frac{1}{\sqrt{2}}(x_1' - x_2'), \text{ whence}$$

$$p_2 = \frac{1}{\sqrt{2}}(p_1' - p_2') \quad (A4.3)$$

By substitution from (A4.3), Eq. (A4.1) and (A4.2) become

$$U_{kin} = \frac{1}{2m}(p_1'{}^2 + p_2'{}^2)$$

$$U_{pot} = \tfrac{1}{2}\left(k - \frac{2q^2}{r^3}\right) x_1'{}^2 + \tfrac{1}{2}\left(k + \frac{2q^2}{r^3}\right) x_2'{}^2$$

$$(A4.4)$$

These correspond to the kinetic and potential energies of two uncoupled oscillators with the force constants

$$k_1 = k - \frac{2q^2}{r^3}, \quad k_2 = k + \frac{2q^2}{r^3}. \quad (A4.5)$$

---

[10] In many mechanical systems the potential energy is expressible as a quadratic form, containing cross-products, in the coordinates; and the kinetic energy is expressible as a sum of squares of the conjugate momenta. It is then always possible, and it is usually advantageous, to make a linear transformation of the coordinates, such that the potential energy becomes a sum of the squares of the new coordinates and the kinetic energy is still a sum of the squares of the new conjugate momenta. Important examples appear in elastic theory and in the theory of specific heats.

Hence the frequencies of these oscillators are

$$\nu_1 = \frac{1}{2\pi}\sqrt{\frac{1}{m}\left(k - \frac{2q^2}{r^3}\right)},$$

$$\nu_2 = \frac{1}{2\pi}\sqrt{\frac{1}{m}\left(k + \frac{2q^2}{r^3}\right)} \quad (A4.6)$$

Now the zero-point energy of the two uncoupled oscillators[11] is

$$E = \tfrac{1}{2}h\nu_0 + \tfrac{1}{2}h\nu_0 = h\nu_0. \quad (A4.7)$$

Similarly, the zero-point energy of the two coupled oscillators is

$$E' = \tfrac{1}{2}h\nu_1 + \tfrac{1}{2}h\nu_2. \quad (A4.8)$$

Since the coupling is weak, the quantity $2q^2/r^3$ must be small compared to k. Then the value of (A4.8) can be found by expanding the expressions (A4.6) in power series in $2q^2/kr^3$. Use of the series expansions

$$\sqrt{1 \pm a} = 1 \pm \frac{a}{2} - \frac{a^2}{8} \pm \frac{a^3}{16} - \dots, (A4.9)$$

yields the new zero-point energy

$$E' = h\nu_0\left(1 - \frac{q^4}{2k^2 r^6} - \dots\right). \quad (A4.10)$$

Thus the energy of the coupled system is less than that of the uncoupled system by approximately the value of the second term in the bracket:

$$\Delta E = h\nu_0 \frac{q^4}{2k^2 r^6}. \quad (A4.11)$$

A somewhat more careful analysis, in which the oscillations are not restricted to the line of centers of the atoms but can occur in any direction in space, changes the numerical factor in (A4.11) from $\tfrac{1}{2}$ to $\tfrac{3}{4}$:

$$\Delta E = h\nu_0 \frac{3q^4}{4k^2 r^6}. \quad (A4.12)$$

---

[11] See Wave-Mechanical Properties of Stationary States, a monograph in this series.

The force constant k is related to the polarizability by $k = q^2/\alpha$, as the last chapter showed. Hence Eq. (A4.12) becomes

$$\Delta E = \frac{3h\nu_0\alpha^2}{4r^6}. \qquad (A4.13)$$

Moreover that value of k can be used

in the expression for the frequency, to give

$$\nu_0 = \frac{q}{2\pi}\sqrt{\frac{1}{m\alpha}} \qquad (A4.14)$$

and thus the dispersion energy

$$\Delta E = \frac{3h}{8\pi r^6}\sqrt{\frac{q^2\alpha^3}{m}}. \qquad (A4.15)$$

PROBLEMS

4.1 The tetrahedral molecules of methane, CH_4, are in rotation over much of the temperature range in which methane is solid, and you can regard the solid as made of spheres of radius 2.18 Å, having the same arrangement as that of the atoms in solid argon.

(a) Verify approximately the calculated value of the binding energy shown in Table 4.1.

(b) What "number of electrons" in Eq. (4.4) would give the same result?

4.2 The carbon monoxide molecule is isoelectronic and isobaric with the nitrogen molecule, and has a very small dipole moment. The densities of the solid forms of the two are nearly the same. Assuming that they have the same crystal structure, calculate a value of the binding energy of solid carbon monoxide from that of nitrogen (Table 4.1) for comparison with the experimental value 2.09 kcal per mole. The polarizability of a CO molecule is $1.99 \times 10^{-24}\,cm^3$, and its ionization potential is 329 kcal per mole.

4.3 The density of solid argon is 1.7 and of solid krypton is 3.2, and both adopt the same crystal structure. From these data, the atomic weights, and the data for polarizabilities and ionization poten-

tials in Table 4.1 calculate the binding energy of krypton from that of argon shown in Table 4.1.

4.4 In a more refined calculation than that of the text, the binding energy of crystals held together by dispersion forces must include the repulsive contribution which keeps the atoms apart. For this purpose an expression similar to that in Chapter 3, Eq. (3.1), for ionic crystals can be used. The most convenient is the so-called "Lennard-Jones" or "6-12" potential:

$$U = -\frac{A}{a^6} + \frac{B}{a^{12}},$$

where A and B are constants and a is some characteristic distance in the crystal, such as the nearest-neighbor distance.

(a) If U is the binding energy per mole, what is A for a crystal of atoms of polarizability α and ionization potential I when you take a as the nearest-neighbor distance, consider only nearest-neighbor interactions, and give each atom twelve nearest neighbors.

(b) Find B in terms of A and the equilibrium separation a, and hence correct the calculated value of 4.1 kcal per mole for the binding energy of argon obtained in the text.

So far the discussion of the attractions between atoms has been able to proceed with little recourse to the quantum mechanical description of the behavior of the electrons forming the bonds. By accepting the fact that a sodium atom will tend to lose an electron, and a chlorine atom to gain one, it was possible to examine the bond between the resulting ions by using classical electrostatic ideas. By accepting the fact that the electrons in an atom behave somewhat like a distortable charge-cloud around its nucleus, similar ideas availed in examining the dispersion force between two neutral atoms.

Any examination of the covalent bond, however, comes face to face with the detailed behavior of the electrons that form the bond, and thus with the wave mechanics necessary to describe that behavior. There is much flexibility in the behavior, as the chemical diversity of our world mutely testifies. Chemists have found many rules to help predict and describe the occurrence and character of covalent bonds between the various atomic species, and their science continues to make new discoveries and new formulations.

Instead of detailing their methods and results, the next few chapters will search more physically for the dynamical behavior that enables electrons to form covalent bonds between atoms. We inquire when nuclei and electrons form a stable system in which the nuclei lie close to one another. The cases chosen for examination are the simplest, and they are made even simpler by representing them with plausible models. This chapter in particular will carry that procedure almost to absurdity: its models, though plausible, will be wrong. Often an examination of a plausible idea, which turns out to be wrong, helps to make clear what is right.

Characteristically a covalent bond between two atoms is an electron-pair bond; two electrons of opposite spin are in states described by wave functions that have the same shape. But a bond formed by only one electron has most of the same physical characteristics. Look first, therefore, at a one-electron bond - in particular at the simplest instance of it, the hydrogen molecule-ion, H_2^+.

The hydrogen molecule-ion composed of two protons, each with charge $+e$, and one electron with charge $-e$, is an observable species of matter. There are good experimental values of the average separation of the two protons in the ground state of the molecule - the bond length R_0 - and of the (negative) energy of the molecule in that state relative to a zero of energy in which the two protons and the electron are all far from one another and at rest - the binding energy U_0.[12]

It is easy to guess roughly what the behavior of this system will be. If the protons are anywhere near each other, the electron will be attracted by both protons and will describe some orbit about them. The protons, each with a mass 1840 times the mass of the electron, will be relatively sluggish in responding to the pull of the rapidly moving electron. But if the electron spends more time between than away from them, it will pull them toward each other on the average. As they approach each other, their positive charges will repel each other more and more, and furthermore the

_____

[12]"Binding energy" is a term used somewhat loosely, and this monograph is no exception. In this chapter it will mean the energy required to disperse the electrons and nuclei to great distances, and will be distinguished from the "dissociation energy" required to disperse the ingredients of a molecule or a crystal into widely separated atoms or ions.

electron will have less and less space
between them in which to spend time.
For both these reasons the protons
will find some separation R_o at which
these competing effects balance.

To examine this system exactly,
however, offers a problem in the dy-
namics of three charged particles, in-
teracting according to Coulomb's law
(Fig. 5.1) - an instance of the famous
three-body problem. Even in classical
mechanics, to say nothing of wave me-
chanics, it has not been solved ana-
lytically. The first approximation to
introduce is suggested by the expecta-
tion that the relatively heavy protons
will move so much less rapidly than
the electron that they will be respond-
ing primarily to a cloud of electronic
charge.

In pursuing this suggestion, one
would first determine what the total
energy of the system would be if the
protons were somehow held fixed at an
arbitrary separation R. That energy
will have three parts: the electrosta-
tic repulsive energy of the fixed nu-
clei, the average kinetic energy of
the moving electron, and the average
potential energy of the electron in
the electrostatic field of the fixed
nuclei. Their sum will be U(R), a func-
tion of R.

Then U(R) can be used to deter-
mine the motions of the protons by
thinking of it as furnishing the po-
tential energy of the proton pair at
the separation R. If U(R) has a mini-
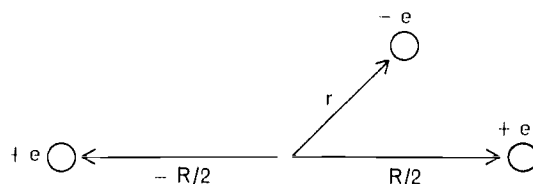mum at some value of R, that value of

Fig. 5.1 The hydrogen molecule-ion contains
two protons and one electron. In a coor-
dinate system whose origin is at the mid-
point between the nuclei, the instantaneous
potential energy of the electron at any
point r, in the field of the nuclei at
$\pm R/2$, is expressed by

$$V(\vec{r}) = - e^2/|\vec{r} - \vec{R}/2| - e^2/|\vec{r} + \vec{R}/2|$$

R is the R_o sought, and that value of
U is U_o, and the system can be ex-
pected to oscillate about the separa-
tion R_o.[13]

Thus the electronic part of the
present three-body problem is reduced
to a one-body problem. But the func-
tion U(R) for the hydrogen molecule-
ion still cannot be expressed in
closed form in terms of well-known
tabulated functions: its values must
be obtained by numerical integration
of a differential equation. More in-
sight into the three contributions to
U(R) comes from examining simplified
models.

The first contribution - the po-

[13]This method of dividing up problems in the be-
havior of systems of electrons and nuclei,
called the "Born-Oppenheimer approximation,"
was introduced by Max Born and J. R. Oppenheimer,
working together in Göttingen in 1927.

SHAPE
OF WELL   a   b   c
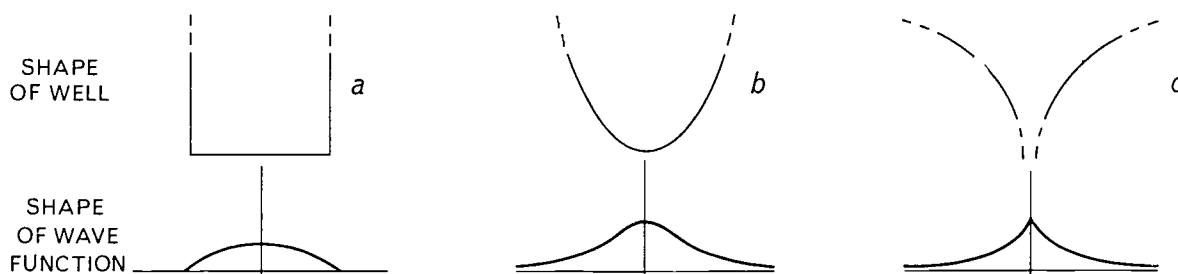
SHAPE
OF WAVE
FUNCTION

Fig. 5.2 In a potential well with a single
minimum, the wave function for the ground
state has a single maximum. The wells above
are for (a) the one-dimensional box, (b)
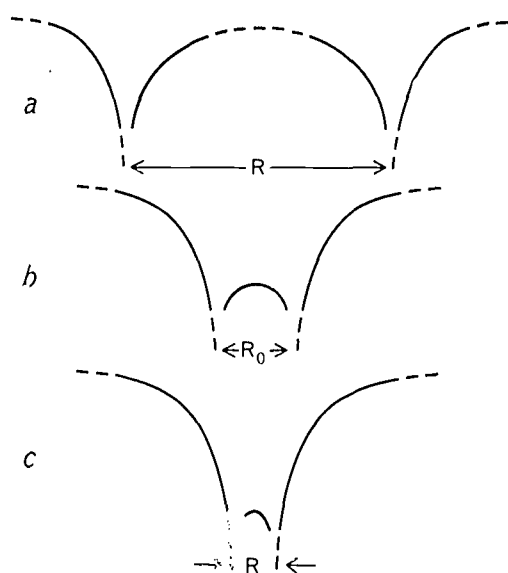the one-dimensional harmonic oscillator,
and (c) an atom, in cross section.

Fig. 5.3   The potential well, shown in cross
section for the electron in the hydrogen
molecule-ion, has two minima. As the dis-
tance R between the nuclei decreases, the
well approaches more nearly the single well
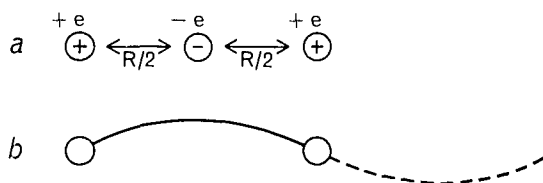offered by a single nucleus.

Fig. 5.4   A suggested approximation (a) for
the average potential energy of the elec-
tron in a hydrogen molecule-ion places the
electron midway between the nuclei, and
(b) for the average kinetic energy uses
a de Broglie wavelength of twice the dis-
tance between the nuclei.
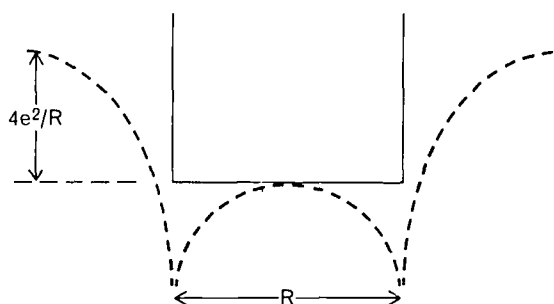
Fig. 5.5   Using the one-dimensional model
of the hydrogen molecule-ion shown in Fig.
5.4 is equivalent to thinking of the elec-
tron as in a box whose width R is the same
as the separation of the protons.

tential energy of the nuclei - is
clearly

$$U_{nuc} = \frac{e^2}{R}. \qquad (5.1)$$

To find the contributions of the kine-
tic and potential energies of the elec-
tron, begin by lumping them together.
The electron is assumed to be bound
by a _potential well_. Its state is as-
sumed to be the ground state described
by solving Schroedinger's equation.
The energy E(R) of that state is the
total energy - kinetic plus potential
- of the electron, and hence

$$U(R) = E(R) + \frac{e^2}{R}. \qquad (5.2)$$

In order to picture what the
ground state might look like, compare
this potential well with some others,
shown in Figure 5.2 (see preceding
page), that are simpler: (a) the
square well, (b) the parabolic well,
and (c) the well offered to an elec-
tron by a single nucleus. The wave
functions for the ground state of a
particle in all these wells have a
roughly similar form: all reach a max-
imum at the middle of the well.[14]

The shape of the potential well
offered to an electron by two nuclei
depends, of course, on the distance
between the nuclei. As Figure 5.3
shows, the nuclei offer two wells,
each quite like Figure 5.2c when they
are far apart (a), and one well of
the same sort when they are very close
together (c). At an intermediate dis-
tance (b) the well looks roughly like
a box with walls of finite height.

That comparison suggests the fol-
lowing crude approximation to the
facts. Assume that the average poten-
tial energy of the electron will be
roughly that of an electron at rest
midway between the nuclei; and assume
that the average kinetic energy of the
electron will be roughly that of a
free particle whose de Broglie wave-

---

[14]The wave functions for some of these wells are
discussed in _Wave-Mechanical Properties of Sta-
tionary States_, a monograph in this series.

Discussion 5.1

A SIMPLE MODEL OF A ONE-ELECTRON BOND

If the wavelength of the electron is $\lambda = 2R$ (Fig. 5.4b), the de Broglie relation for the momentum, $p = h/\lambda$, gives $p = h/2R$ and thus the kinetic energy

$$U_{kin} = \frac{p^2}{2m} = \frac{h^2}{8mR^2}. \qquad (D5.1)$$

If the electronic potential energy is as represented in Fig. 5.4a,

$$U_{pot} = \frac{-e^2}{R/2} - \frac{e^2}{R/2} = \frac{-4e^2}{R}. \qquad (D5.2)$$

Hence the total electronic energy is

$$E(R) = U_{kin} + U_{pot} = \frac{h^2}{8mR^2} - \frac{4e^2}{R}, (D5.3)$$

and the total energy of the system (neglecting any kinetic energy of vibration of the nuclei) is

$$U(R) = \frac{h^2}{8mR^2} - \frac{3e^2}{R}. \qquad (D5.4)$$

By differentiating $U(R)$ with respect to R, a minimum is found at

$$\frac{-h^2}{4mR_o^3} + \frac{3e^2}{R_o^2} = 0, \text{ or } R_o = \frac{h^2}{12me^2}. \quad (D5.5)$$

At this value of R_o, Eq. (D5.4) yields

$$U_o = - \frac{18me^4}{h^2}. \qquad (D5.6)$$

When the values

$$h = 6.62 \times 10^{-27} \text{ erg-sec},$$
$$e = -4.80 \times 10^{-10} \text{ esu},$$
$$m = 9.11 \times 10^{-28} \text{ g},$$

are put into (D5.5) and (D5.6), they yield the values $R_o = 1.74$ Å, $U_o = -12.3$ eV, to be compared with the experimental values, 1.06 Å and -16.3 eV.

length λ is twice the distance between the nuclei. Figure 5.4 pictures the two ingredients of this guess. As Figure 5.5 shows, the guess corresponds to a one-dimensional model. In that model the electron is in a one-dimensional box whose bottom represents the electron's potential energy when it is midway between the nuclei, and whose sides confine the electron to the line between the nuclei.

The appropriate calculations for this model are carried out in Discussion 5.1. The electronic potential energy goes down as $1/R$, just as the ionic potential energy does in the calculations for the ionic bond in Chapter 3. The electronic kinetic energy goes up as $1/R^2$, behaving somewhat like the repulsive energy in Chapter 3. Thus, as in that earlier work, the energy passes through a minimum as R varies. In this case the minimum yields the values $R_o = 1.74$ Å

and $U_o = -12.3$ eV. Since the experimental values for the hydrogen molecule-ion are $R_o = 1.06$ A and $U_o = -16.3$ eV, the agreement is rather good for so crude a model.[15]

But you can easily get from this model a misconception of the roles which the three ingredients of U(R) play in the actual case. In the model there is a minimum in U(R) only because the electronic kinetic energy increases more rapidly at small R than the total potential energy of the electron and the nuclei decreases. Hence in the model the factor that keeps the nuclei apart is the electronic kinetic energy.

In the real case, Figure 5.3

---

[15] The agreement becomes less impressive on comparing the dissociation energies - the energy of the molecule-ion relative to the energy of a hydrogen atom and a proton separated from each other - as Problem 5.1 shows.

shows that the electronic kinetic en-
ergy cannot increase in that way. As
the nuclei get very close to each
other, the electron sees a pair of
charges which more and more closely
resembles the double charge on a hel-
ium nucleus. The only reason that the
electronic kinetic energy increases
indefinitely in the model is because
the model requires the electron to
stay in a box (Figure 5.5) which be-
comes indefinitely small.

     In the real molecule the electron
is not in such a box. As the nuclei ap-
proach each other, the electron spends
more and more time to the left of the
nucleus on the left and to the right
of the nucleus on the right. Thus as
the internuclear distance shortens,

the wavelength of the electron does
not decrease as much, and its kinetic
energy does not increase as much, as
the model suggests. And since the
electron spends more and more time
away from the position midway between
the nuclei, its potential energy does
not go down as fast in the fact as in
the model.

     Indeed examining the two extremes
shown in Fig. 5.3a and c makes clear
that, when the nuclei are far apart
(a), the total electronic energy will
be that of the hydrogen atom, for the
electron will be on one nucleus or the
other; and when the nuclei coincide
(c), the total electronic energy will
be that of the helium ion, He^+. Since
the energy of an electron in the
ground state of a one-electron atom
varies as $-Z^2$, where Z is the atomic
number of the atom, the total elec-
tronic energy E(R) must go down
smoothly by a factor of 4 as R de-
creases from R = ∞ to R = 0. Clearly
what finally keeps the nuclei apart
in the hydrogen molecule-ion must be
their electrostatic repulsion U_{nuc},
not the electronic kinetic energy. The
calculated model yields an approxima-
tion to the correct internuclear dis-
tance and binding energy only by good
fortune.

     Since this model has the major
defect of confining the electron too
closely to the space between the nu-
clei, consider another one-dimensional
model which avoids this defect - a
"delta-well model." A "delta well" - a
well that is infinitesimally wide but
infinitely deep - affords one bound
state for a particle.[16] As the width
ℓ of the well approaches zero, and
the potential energy V of a particle
in the well becomes negatively infi-
nite, in such a way that the product
$V\ell = -\eta$ remains finite, then the en-
ergy of the electron in the bound
state takes the form $-E = \eta^2/4$, and

_____

[16]The properties of a particle in the presence
of a delta well are examined in The Nature of
Atoms, a monograph in this series.

its wave function to the left and the right of the well is

$$\psi_\ell = Ae^{\eta x/2}, \quad \psi_r = Ae^{-\eta x/2}. \quad (5.3)$$

Thus the wave function for an electron in the presence of the well looks like Fig. 5.6: it has the same form as a one-dimensional cross section of the wave function for the ground state of the hydrogen atom. This correspondence suggests using two such wells to make a one-dimensional model for examining the ground state of the hydrogen molecule-ion.

The model is simple enough for exact calculation: an appendix to this chapter carries out the formalities, finding two different possible states for the electron. In one state the wave function is symmetrical about the midpoint between the two wells, and in the other state the wave function is antisymmetrical, as Fig. 5.7 shows. The energy of a particle in either of these states approaches the same value as the distance between the nuclei becomes very large. For an electron whose wave function has the symmetrical form, the energy decreases in the expected way from that of the hydrogen atom to that of the helium atom as the nuclei come together. For the antisymmetrical wave function, however, the corresponding energy increases as the separation between the nuclei is reduced. These energies are plotted as functions of R in Fig. 5.8.

Notice a rough analogy between what is happening here and what happens to two harmonic oscillators that are coupled by a weak spring, described in the last chapter. When the nuclei are far apart, the two electronic states are analogous to two identical oscillators that are uncoupled. Each nucleus affords a bound state for the electron; the two states are identical except that they are located in two different places, and both wave functions give the electron an even chance of being at either nucleus. When the nuclei are infinitely separated, the squares of the symmetrical and antisymmetrical wave functions

will be the same, and thus give the same probability distribution for the electron. As the nuclei come closer to each other, the energy level is split, in a way similar to the splitting described in the last chapter for
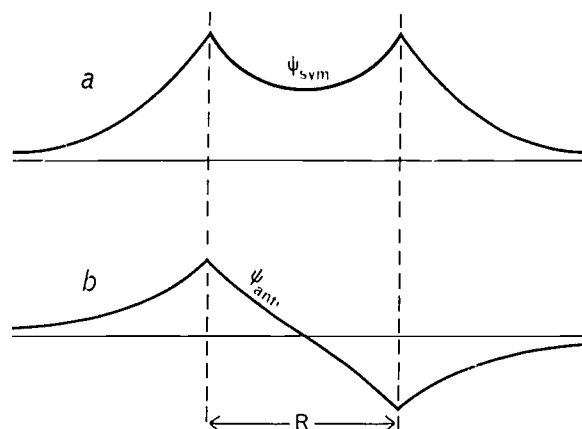

Fig. 5.7 A pair of delta wells, separated by a distance R, affords two bound states for a particle, whose wave functions are, respectively, symmetrical and antisymmetrical about the midpoint between the wells.
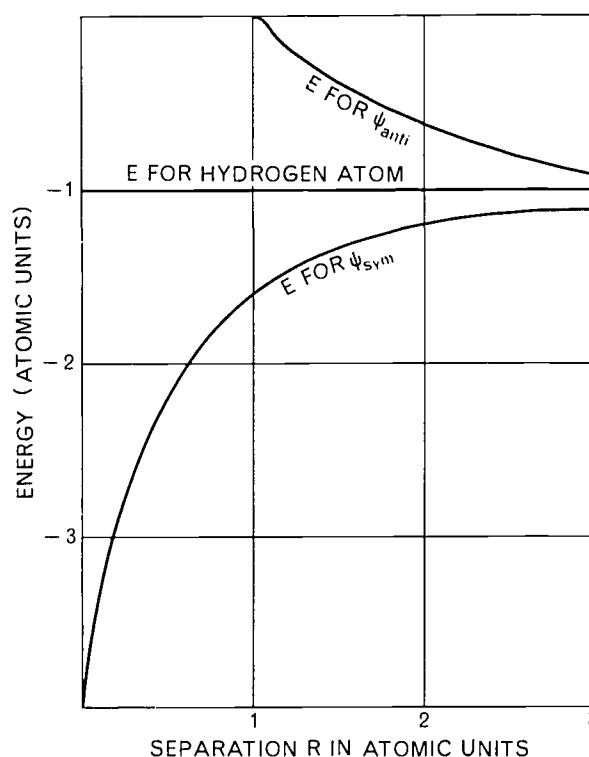

Fig. 5.8 The energies of an electron in the two states afforded by two delta wells, as functions of the distance between the wells.

the frequencies of the two identical
oscillators when they are coupled. You
may find it helpful to think of the
two identical states, afforded by the
nuclei, as coupled and thus providing
two states with properties that differ
increasingly as the coupling is in-
creased by decreasing the nuclear
separation.

Clearly an electron whose wave
function has the antisymmetrical form
cannot provide a stable bond for the
molecule, for both the electronic and
the nuclear repulsive energies in-
crease monotonically with decreasing
nuclear separation. An electron in the
symmetical wave function might give
bonding - since $E(R)$ decreases mono-
tonically with the nuclear separation
R - if the sum $U(R)$ of $E(R)$ and the
nuclear repulsive energy, goes through
a minimum. As the appendix shows, that
sum does not go through a minimum for
this model, but increases monotoni-
cally, though of course the sum is
less than the corresponding sum for
the antisymmetrical case.

Thus again the model is a poor
one, and hindsight shows why. The two
delta wells provide potentials with-
out any "range": the electron experi-
ences a negative potential energy only
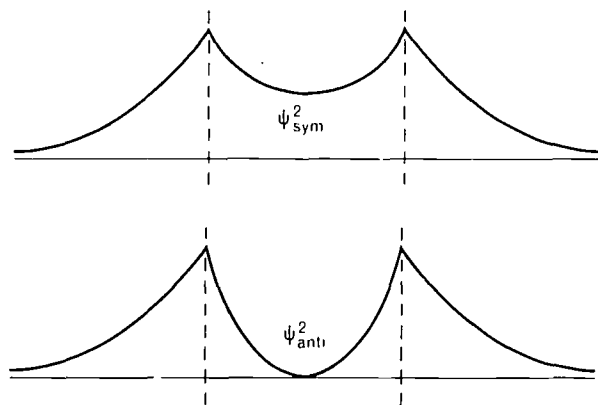when it is precisely at one or another

Fig. 5.9 According to the probability in-
terpretation of wave functions, the squares
of the two functions shown in Fig. 5.7
measure the relative probability of finding
the electron at various places, when it is
in a state described by one or the other
wave function.

of the "nuclei," no matter what the
separation R of the "nuclei" may be.
At the same time the model retains,
for the nuclear repulsive energy, the
long range of the Coulomb potential.
In the real case, the potential energy
of the electron when it is between the
nuclei keeps going down as the nuclei
come toward each other (Figure 5.3).
Hence in reality it is increasingly
favorable for the electron to take a
position between the nuclei, where it
will attract both nuclei toward itself
and thus toward each other. That in-
creasing tendency is resisted only by
the tendency of the electron to reduce
its kinetic energy by increasing its
de Broglie wavelength.

But even though the model does
not provide a stable bond, it illus-
trates faithfully two important fea-
tures of a real molecule: (1) the
formation, from the atomic states of
the two atoms, of a symmetrical and
an antisymmetrical state, and (2) the
fact that the symmetrical state is
the one that might afford a bond. The
symmetrical state is often called a
"bonding state" of the electron, and
the antisymmetrical state is called
an "antibonding state." Squaring the
wave functions of Fig. 5.7 for the
two states shows (Fig. 5.9) that the
bonding state gives a higher probabil-
ity of finding the electron between
the nuclei, in agreement with the pic-
ture that bonding is acomplished by
the electrostatic attraction of the
electron for the nuclei while it is
between them.

Indeed that picture is rigorously
correct. It has been shown[17] that the
forces that the electrons in a mole-
cule exert on the nuclei are just
those that would be exerted according
to classical electrostatic theory by
a cloud of negative charge distributed
according to the probability interpre-
tation of the square of the wave func-
tion for the electrons. The equilib-
rium lengths of the bonds are deter-

[17]R. P. Feynman, Phys. Rev. 56, 340 (1939).

mined by the point at which the at-
tractive forces, which this cloud of
negative charge exerts on the nuclei,
are exactly balanced by the electrosta-
tic repulsive forces of the nuclei on
one another. From this point of view,
the duty of wave mechanics is to de-
termine the density of electronic
charge as a function of the space co-
ordinates, for various separations of
the nuclei. Then the rest of the cal-
culation can be carried out by using
classical electrostatic ideas. But at
present the importance of the "force
way" of looking at the problem is con-
ceptual rather than practical. None of
the presently available methods for
calculating bond energies and inter-
atomic distances uses this procedure:
all the methods are "energy methods."

Even though the search in this
chapter for a simple one-dimensional
model for the hydrogen molecule-ion
has yielded none, these trials have
clarified the problem. In the light of
the preceding discussion, you could
easily construct a model that would
embody those ingredients, but you
might have difficulty finding one
that comes usefully close to the facts
and at the same time can be easily
calculated.

What does this study of the hy-
drogen molecule-ion lead you to ex-
pect when the system acquires another
electron and so makes a hydrogen mole-
cule in which the two protons and two
electrons form a stable system? The
two electrons will both be in the
spacially symmetrical state and will
have opposite spins. Then, ignoring
the electrostatic repulsion between
the two electrons for the moment, you
can expect that the electronic energy
will be twice as great as before at
each value of R. Since the nuclear re-
pulsion will be the same as before at
each value of R, the minimum total
energy will lie at a shorter separa-
tion of the nuclei. Thinking in terms
of the forces in the system, you can
expect to find roughly twice as much
negative charge between the nuclei,
tending to pull them together. But you

cannot easily guess what separation
of the nuclei will provide the new
force balance, nor what the total en-
ergy will be at that separation.

Adding the electrostatic repul-
sion between the two electrons will
make additional corrections in your
guess. That interaction will add a
repulsive term to the electronic po-
tential energy. Moreover, by making
the electrons tend to stay out of
each other's way, it will reduce the
electronic density between the nuclei
and thus reduce the attractive terms
in the electronic potential energy.

In experimental fact, the bond
length in the hydrogen molecule is
0.74 Å, to be compared with 1.06 A
in the molecule-ion. The total energy
of the molecule is -31.7 eV, to be
compared with -16.3 eV in the mole-
cule-ion. At first it may seem sur-
prising how nearly the energy is
doubled by adding the second elec-
tron. The addition of a second elec-
tron to the helium ion, to form the
neutral helium atom, releases less
than half the energy that is released
by the first electron when it joins
the helium nucleus to form the ion.

There is a great quantitative
difference between atoms and mole-
cules in this respect. The effect of
the repulsion between electrons is
more important in an atom because
there a single nucleus is attracting
several electrons to it. In a mole-
cule the separation of the centers of
positive charge gives the several elec-
trons space to move about in a region
of low potential energy, without get-
ting in the way of one another.

In one important way, however,
both the hydrogen molecule and the
molecule-ion fail to typify the be-
havior of other molecules. Only in
these two molecules are the atoms held
apart entirely by the electrostatic
repulsion between their nuclei. In all
other molecules the repulsive force
arises primarily from the behavior of
the electrons that are not engaged in
bonding. As the atoms come closer to
each other, those disengaged electrons

are forced into states of higher energy, and so offer a strong repulsion to closer approach. As you saw in Chapter 3, that repulsion grows in strength much more rapidly with decreasing separation than the electro-

static repulsion that keeps the protons apart in the hydrogen molecule. Pursuing in the next two chapters a more penetrating analysis of the electron-pair bond, you will see the origin of that repulsion more clearly.

PROBLEMS

5.1 The energy of the hydrogen atom in its ground state is minus one atomic unit, or -13.58 eV. That is the energy of the atom relative to a proton and an electron infinitely separated and at rest. What is the difference in energy between H_2^+ and $H + H^+$? In other words, is the hydrogen molecule-ion stable or unstable relative to one hydrogen atom and one proton infinitely separated, and by how much energy? This quantity is called the "dissociation energy" of the molecule. Compare the experimental value with the value calculated in Discussion 5.1.

5.2 The virial theorem asserts that, in a system of charged mass-points interacting by Coulomb's law, the kinetic energy will be one half the absolute value of the (negative) potential energy when the system is behaving stably. Does the approximation of Discussion 5.1 obey this theorem at the equilibrium separation?

5.3 By looking at the general form of the true wave function for the electron in H_2^+ (for example, Fig. 5.7), you can see that you have been able to get as good an approximation as you have by the crude model of Figs. 5.4 and 5.5 in consequence of making two errors that partially compensate each other. What is the nature of these errors?

5.4 It might occur to you that the delta-well model for H_2^+ contains a conceptual inconsistency (in using the short-range potential of the delta well for the electron-proton interactions, and the long-range Coulomb potential for the proton-proton interactions) which could be removed by representing the proton-proton interaction as a delta spike. Conclude without calculation what internuclear distance, and what total energy, you would obtain as equilibrium values.

Appendix   A DELTA-WELL MODEL OF THE HYDROGEN MOLECULE-ION

To find the wave functions for an electron moving in one dimension, in the presence of two delta wells separated by the distance R (Fig. 5.10), write Schroedinger's equation. When written in atomic units,[18] it is

---

[18]This method of simplifying the appearance of Schroedinger's equation is described in <u>Wave-Mechanical Properties of Stationary States</u>, a monograph in this series.

$$\frac{d^2 \psi}{dx^2} + \left[E - V(x) \right] \psi = 0. \qquad (A5.1)$$

Everywhere outside the wells $V(x) = 0$, and thus for the three ranges of Fig. 5.10 the appropriate solutions are of the form

$$\psi_1 = A e^{kx}, \quad \psi_3 = B e^{-kx},$$

$$\psi_2 = A_2 e^{kx} + B_2 e^{-kx}, \qquad (A5.2)$$

where $k \equiv \sqrt{-E}$, and E is negative when the electron is bound to the wells. Matching ψ_1 to ψ_2 at $x = -R/2$, and ψ_2 to ψ_3 at $x = +R/2$, gives

$$A = A_2 + B_2 e^{kR}$$

$$B = B_2 + A_2 e^{kR}. \qquad (A5.3)$$

At each well the function will have a discontinuity of slope, obtainable by integrating Eq. (A5.1) across the well, and taking the well so narrow that ψ is constant over its width ℓ, and so deep that E is negligible in comparison with V. With the use of these assumptions, Eq. (A5.1) becomes

$$d \frac{d\psi}{dx} = V\psi dx. \qquad (A5.4)$$

Then at the left well

$$\frac{d\psi_2}{dx}\bigg|_{x = -R/2} - \frac{d\psi_1}{dx}\bigg|_{x = -R/2} = \psi(-R/2)V\ell,$$

$$(A5.5)$$

and at the right well

$$\frac{d\psi_3}{dx}\bigg|_{x = R/2} - \frac{d\psi_2}{dx}\bigg|_{x = R/2} = \psi(R/2)V\ell.$$

$$(A5.6)$$

Evaluating (A5.5) and (A5.6), and denoting $V\ell \equiv -\eta$ (where η is positive since V is negative), yields

$$A_2 k - B_2 ke^{kR} - Ak = -\eta A,$$
$$B_2 k - A_2 ke^{kR} - Bk = -\eta B. \qquad (A5.7)$$

When A and B are eliminated from (A5.7) by using (A5.3),

$$\eta A_2 = (2k - \eta) B_2 e^{kR},$$

$$\eta B_2 = (2k - \eta) A_2 e^{kR}, \qquad (A5.8)$$

whose consistency requires

$$e^{kR} = \frac{\pm\eta}{2k - \eta}. \qquad (A5.9)$$
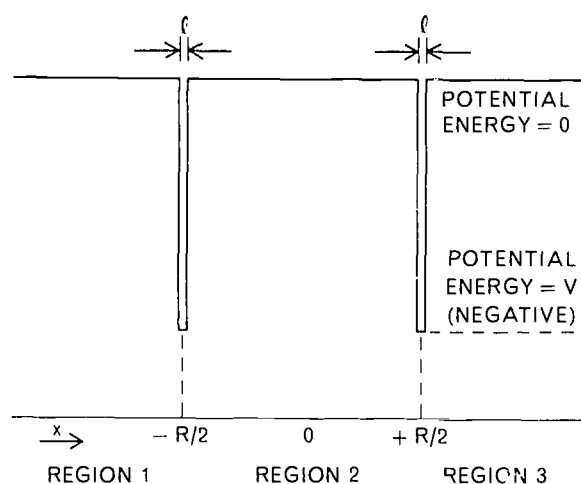
When $e^{kR} = +\eta/(2k - \eta)$, Eqs.

Fig. 5.10   In the delta-well model for the hydrogen molecule-ion, the potential for the electron due to the two protons is simulated by two square potential wells in which $\ell \to 0$ and $V \to -\infty$ in such a way that $-V\ell = \eta$, a positive constant.
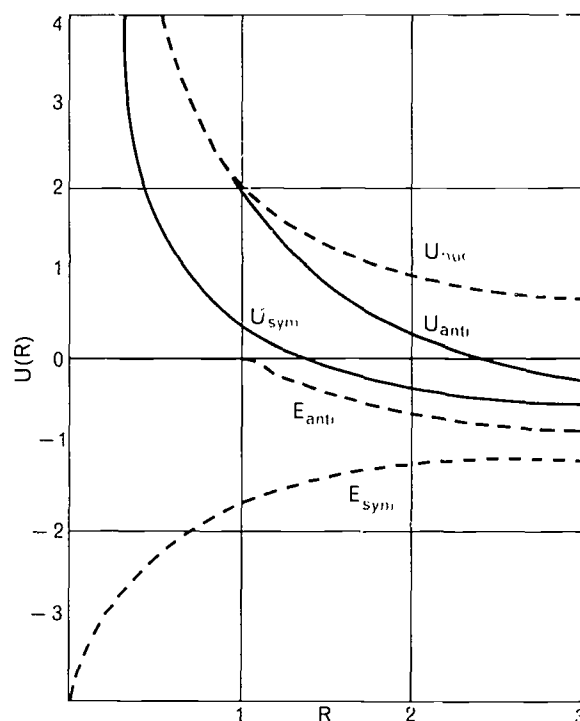

Fig. 5.11   The total energy, and its components, in the delta-well model of the hydrogen molecule-ion, when the electron is in the symmetric and antisymmetric bound states, plotted in atomic units.

(A5.8) give $A_2 = B_2$, and hence by
(A5.3) $A = B$. In this case, therefore,
ψ is symmetric about $x = 0$. When
$e^{kR} = -\eta/(2k - \eta)$, Eqs. (A5.8) give
$A_2 = -B_2$, and hence by (A5.3) $A = -B$.
In this case ψ is antisymmetric about
$x = 0$. In the symmetric case, when
$R = 0$, $k = \eta$, or $E = -\eta^2$. As R in-
creases, k aecreases, remaining
greater than $\eta/2$, and as $R \to \infty$,
$k \to \eta/2$, or $E \to -\eta^2/4$.

In the antisymmetric case $k < \eta/2$
for large R, and thus as $R \to \infty$,
$k \to \eta/2$ again. As R decreases, so does
k, and at the point where k goes
through zero and becomes negative, the
exponential forms of solution (A5.2)
are no longer acceptable, since they
would cause the wave function to in-
crease indefinitely for large posi-
tive and negative values of x. Thus
for small separations, E will be posi-
tive, and Eq. (A5.1) will have trigo-
nometric solutions, describing an
electron that is not bound to the
wells but suffers a change in phase
in its wave function as it traverses
the wells. The value of R at which
this transition occurs can be found by

expanding both sides of (A5.9) for the
antisymmetric case in powers of k,

$$1 + kR + \ldots = 1 + \frac{2k}{\eta} + \ldots, \quad (A5.10)$$

and finding

$$R \to 2/\eta \text{ as } k \to 0.$$

In order to specialize the prob-
lem to the hydrogen molecule-ion, take
$\eta = 2$, since the energy of the ground
state of the hydrogen atom is -1
atomic unit, and $-E \equiv k^2 = \eta^2/4$ for
the infinitely separated wells. The
value of R obtained from (A5.9) is

$$R = \frac{1}{k} \log \frac{\pm 1}{k - 1}. \quad (A5.11)$$

The plots of Fig. 5.8 can now be made
by using this value of R and the value
$E(R) = -k^2$. Since the nuclear repul-
sive energy is e^2/R, or $2/R$ in atomic
units, $U(R)$ can now be plotted against
R (Fig. 5.11) (see preceding page) in
atomic units, to find that the delta
wells fail to provide a true bonding
state, for the reasons the text dis-
cusses.

The covalent bond between two atoms can be understood quite well by examining the behavior of a single electron in the presence of two attracting nuclei, as the last chapter pointed out. But the covalent bond is usually formed by two electrons, not one; and the end of the last chapter suggested a way of thinking about how those two electrons behave. It pictured the two electrons in states described by wave functions that show the same spacial dependence, and in which the electrons have opposite spins.

Now this is a rather loose way of thinking about two electrons: it says both more and less than can properly be said about them. For example, by putting each electron separately into a one-electron state, this way of thinking offers no way of estimating the effect of their mutual repulsion, and thus it provides less information than you have a right to ask. On the other hand, by putting both electrons into states with the same spacial dependence, and retaining the exclusion principle, it forces the conclusion that the two electrons must have opposite spins. They usually do, to be sure, but in many important cases - the oxygen molecule, for example - they do not.

These difficulties have arisen out of a mistake that marks this way of thinking about the pair of electrons. We have considered the electrons too much as two, and too little as a pair. Electrons are indistinguishable particles. One can say how many there are, but one can find no labels that will identify which is which. In consequence, one must examine wave functions that describe states for both electrons together, and one must require that such a wave function should give the same description of a state if the two electrons are interchanged.

It is not difficult to embody this idea in a mathematical program; it is difficult only to carry through the calculations that the program prescribes. Schroedinger's equation again provides the necessary mathematical apparatus.[19] In the present context it is a partial differential equation whose single dependent variable is the desired wave function - a function of the coordinates of both electrons. The part of the equation that contains the potential energy of the electrons includes the instantaneous potential energy of each in the presence of the two nuclei, and also the instantaneous repulsion between them. The solutions that are picked out as physically meaningful are those whose squares retain the same value when the coordinates of the electrons are interchanged.

In order to see what the product of such a program might be, look for a moment at the result it would yield when applied to the simple one-dimensional model of the last chapter. Again the two electrons are confined to a line, and two delta wells simulate the attraction of the two nuclei. Representing the positions of each delta well along the line by $\oplus$, Fig. 6.1 (see next page) repeats the forms of the two wave functions of lowest energy that were found for one electron in the last chapter. For two electrons the wave function now becomes a function of two variables - the instantaneous positions of the two electrons along the line - and must therefore be plotted as hills and valleys above and below the plane shown in Fig. 6.2 (see next page). The square of its value at any point in the plane measures the relative probability that the

---

[19]The procedure is described in Wave-Mechanical Properties of Stationary States, a monograph in this series.

two electrons will be simultaneously
at the places represented by the point.
The dashed line marks the points that
represent the coincidence of the two
electrons at one and the same place.

One of the wave functions for
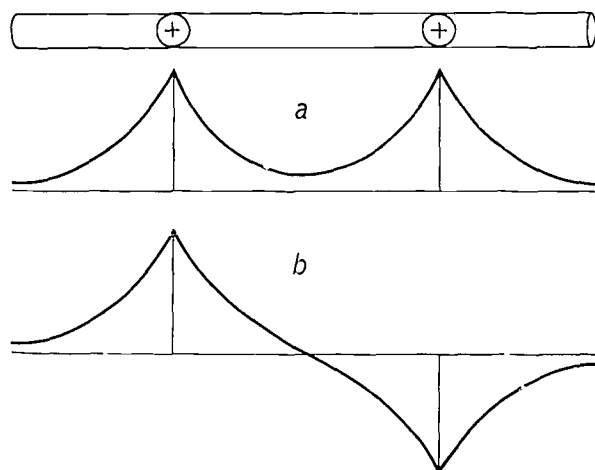this system is shown in Fig. 6.3. The

Fig. 6.1   For the delta-well model of the
hydrogen molecule-ion in Chapter 5, the
two one-electron wave functions are spaci-
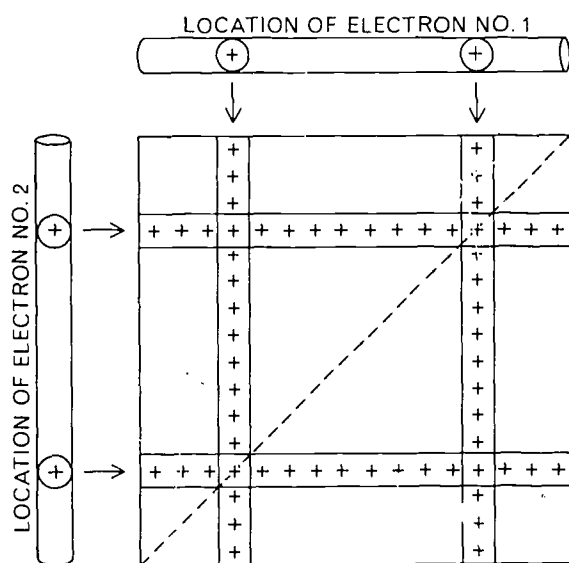ally symmetrical (a) and antisymmetrical (b).

LOCATION OF ELECTRON NO. 1

Fig. 6.2   Specifying the positions of the
two electrons in the one-dimensional delta-
well model of the hydrogen molecule re-
quires a plane instead of a line. The re-
gions marked + show the positions of the
wells, and the dashed line shows the points
at which the two electrons are coincident.

electronic probablity is highest near
the attracting wells, and some of
that probability is pushed away from
the places where the electrons are
near each other. The wave function is
symmetric to a reflection across the
dashed line, in obedience to the re-
quirement that the square of its value
will not change if the electrons are
interchanged.

Another wave function, satisfy-
ing all the requirements mentioned so
far, is shown in Fig. 6.4. Unlike that
shown in Figure 6.3, it is antisym-
metric to reflection across the dashed
line: interchanging the electrons
changes its sign. But since its square
is symmetric, it still makes the same
predictions of probability when the
two electrons are interchanged, and
therefore it is entirely acceptable.

Entering the argument at this
point, however, is the behavior of
electrons that is codified in the ex-
clusion principle. Clearly the prin-
ciple cannot be taken here in the
simple form that it has taken in ear-
lier arguments about how two electrons
occupy two one-electron wave functions.
In this context the exclusion princi-
ple must be given its more general
form - the form from which the more
familiar form can be derived as a con-
sequence in cases where one-electron
wave functions provide an adequate ap-
proximation.[20] As Discussion 6.1 (see
page 42) describes, the exclusion prin-
ciple asserts for the case now at hand
that the two electrons in the spa-
cially symmetrical wave function (Fig.
6.3) will have opposite spins, and in
the spacially antisymmetric wave func-
tion (Fig. 6.4) will have spins in the
same direction.

From this point of view, there-
fore, the fact that the electrons in
an electron-pair bond usually have op-
posite spins is due to the fact that
in most real cases the state with the
spacially symmetrical wave function

[20]The general form of the exclusion principle
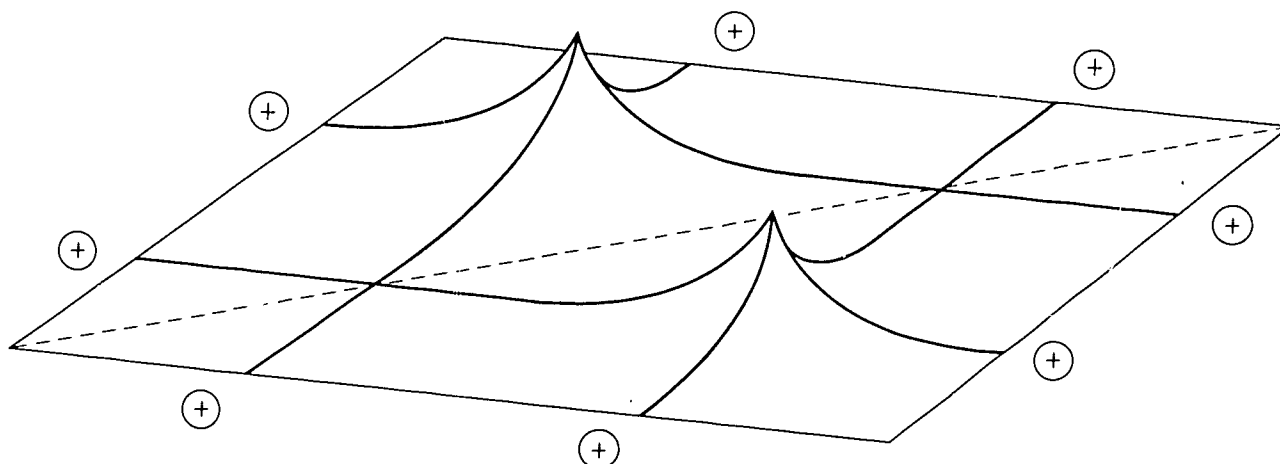is discussed in Wave-Mechanical Properties of
Stationary States.

Fig. 6.3 The spacially symmetrical wave function for the two electrons in the delta- well model of the hydrogen molecule has two peaks, for electrons at different wells.
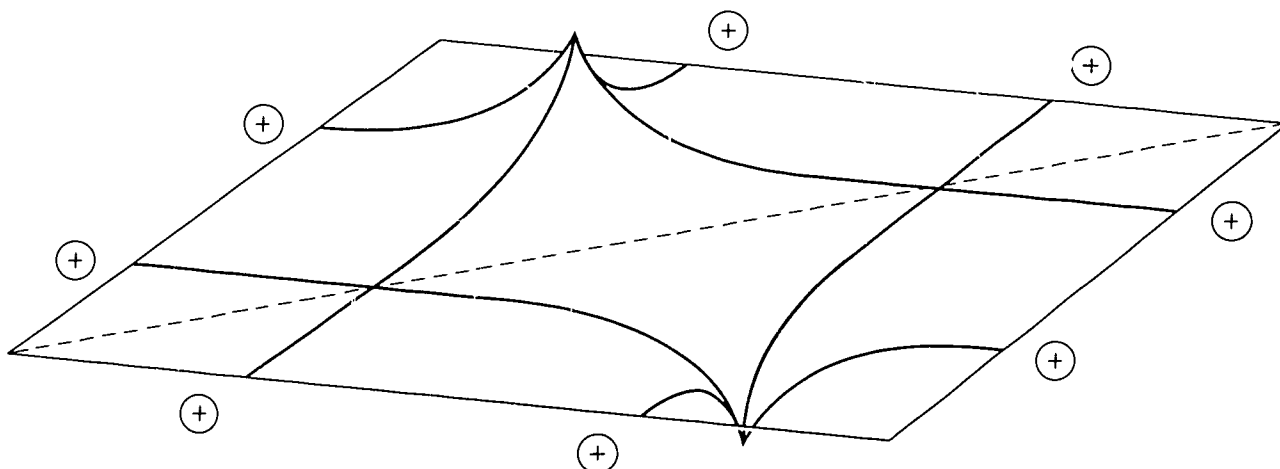

Fig. 6.4 The spacially antisymmetrical wave function for the two electrons in the delta-well model of the hydrogen molecule has two "peaks" that are of opposite senses.

has the lower energy. But there are cases, such as oxygen, in which the spacially antisymmetrical wave function corresponds with the lower energy. And in any case, the electrons in some bond in a molecule may be excited by outside influences into a state of higher energy that is spacially antisymmetrical, and thus a pair of electrons may exhibit parallel instead of antiparallel spins.[21]

In order to make qualitative calculations, an electron-pair bond is often approximated by thinking of it as a suitable combination of the states that the two electrons would have on the two bonded atoms if the atoms were entirely separate. There are two ways of constructing such an approximation. The first method proceeds by taking an atomic wave function on each of the two atoms, placing an electron in each, and then bringing the atoms closer together. The second method makes linear combinations of the two atomic wave functions, each approximating a wave function for the bond such as the last chapter depicted, and then puts in the electrons one after the other. The rest of this chapter examines the application of both these methods to the electron-

---

[21] For spectroscopic reasons, such a state is usually called a "triplet state."

Discussion 6.1

THE PRINCIPLE OF ANTISYMMETRY

The two-electron wave pictured in
Fig. 6.3 is "symmetric to the inter-
change of the electrons," because the
picture is unaffected by imagining
that the electrons have exchanged
places. When the pair of electrons is
in that state, the exclusion principle
asserts that their spins will be op-
posite. On the other hand, if the two
electrons in the wave of Fig. 6.4 ex-
change places, the wave is turned up-
side down: every positive number de-
scribing the height of its hills and
valleys is made negative, and every
negative number is made positive. Such
a wave is said to be "antisymmetric
to the interchange of the electrons."
And in that case the exclusion prin-
ciple asserts that their spins will be
parallel.

A single rule will cover both
cases. Put a number - say, the number
one - to the spin of an electron.
Then the spin of another electron re-
ceives the same number if it is in the
same direction, and the number minus
one if it is in the opposite direc-
tion. Multiplying the two numbers for
the spins of the two electrons gives

+1 if the spins are parallel, −1 if
the spins are opposed. Now include, as
part of the operation of interchanging
the electrons, the operation of multi-
plying their wave by +1 or −1 (+1 if
their spins are the same, −1 if their
spins are opposed). Then the inter-
change turns the waves of both Figs.
6.3 and 6.4 upside down. In both cases
the wave can be called antisymmetric
to the interchange of the electrons.

In a fashion such as this, the
exclusion principle can be extended to
waves for many electrons. The more
general form of the principle contin-
ues to assert that electrons are found
only in antisymmetrical states, when
their spins are included in the de-
scription of their states.

The theory of this property of
electrons predicts that no event, of
any sort familiar to us, could ever
remove electrons from antisymmetric
states and put them into symmetric
states. But the theory also shows that,
if instead the electrons had started
life in symmetric states, no event
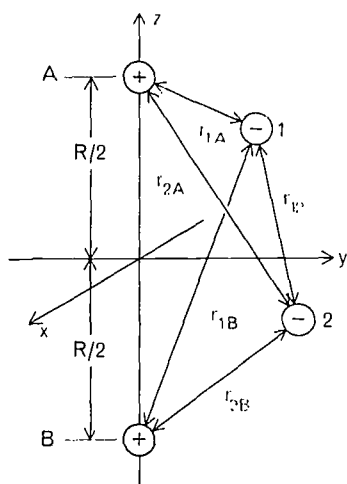could put them into antisymmetric
states.

Fig. 6.5   Coordinates for the problem of
the electron-pair bond in the hydrogen
molecule.

pair bond between the two protons in
the hydrogen molecule.

In preparation for pursuing the
first method, diagram and label a pic-
ture of the contents of the hydrogen
molecule as in Fig. 6.5. The electrons,
No. 1 and No. 2, will have states
whose wave functions are combinations
of the 1s wave functions for two separ-
ate hydrogen atoms.

Two such two-electron states can
be made out of the two 1s functions of
the two atoms. One is symmetric in the
spins and antisymmetric in the space-
dependent part of the function. Call
that space-dependent part ψ_{anti}: in-
terchanging the numbers designating
the electrons in ψ_{anti} will reverse
its sign. The other two-electron state
is antisymmetric in the spins and

Discussion 6.2

TRIAL FUNCTIONS FOR THE HYDROGEN MOLECULE

When the atoms are so far apart that their interaction is negligible, and one electron is on each proton, you can write the Schroedinger equations in atomic units,

$$H_{AB}\ \psi_{AB} \equiv \left[-\nabla_1^2 - \nabla_2^2 - \frac{1}{r_{1A}} - \frac{1}{r_{2B}}\right]\psi_{AB}$$

$$= 2E_H \psi_{AB},$$

$$H_{BA}\ \psi_{BA} \equiv \left[-\nabla_1^2 - \nabla_2^2 - \frac{1}{r_{1B}} - \frac{1}{r_{2A}}\right]\psi_{BA}$$

$$= 2E_H \psi_{BA},$$

depending on which electron is at which proton. Here E_H is one of the energy levels for the hydrogen atom. When they are in their lowest-energy states, both electrons will be in 1s wave functions on their appropriate atoms.

When the atoms interact, you can write, using the coordinates of Fig. 6.5,

$$H\psi \equiv \left[-\nabla_1^2 - \nabla_2^2 - \frac{1}{r_{1A}} - \frac{1}{r_{2B}} - \frac{1}{r_{1B}}\right.$$
$$\left. - \frac{1}{r_{2A}} + \frac{1}{r_{12}}\right]\psi = E\psi.$$

Recalling the method of solving such equations by separation of variables, you know that a solution of the first of these equations is $A(1) \cdot B(2)$, and a solution of the second is $A(2) \cdot B(1)$. Here $A(1)$, for example, denotes the 1s wave function for hydrogen atom A, written for the coordinates of electron number 1. Since the 1s wave function for hydrogen drops off exponentially with r, the wave function $A(1)$, in the coordinate system of Fig. 6.5, and with distances expressed in atomic units, is

$$A(1) = e^{-r_{1A}},$$

$$r_{1A} = \sqrt{x_1^2 + y_1^2 + \left(z_1 - \frac{R}{2}\right)^2}.$$

Out of such solutions the trial functions

$$\psi_{sym} = A(1) \cdot B(2) + A(2) \cdot B(1),$$

$$\psi_{anti} = A(1) \cdot B(2) - A(2) \cdot B(1),$$

are constructed with a view to examining how well they approximate true solutions of the third of the Schroedinger equations shown above.

symmetric (ψ_{sym}) in the space-dependent part. "Antisymmetric in the spins" means that the spins are opposite: interchanging the numbers designating the electrons in the wave function reverses the spins of both. As Discussion 6.2 shows, the desired wave functions might be written:

$$\psi_{sym} = A(1) \cdot B(2) + A(2) \cdot B(1),$$

$$\psi_{anti} = A(1) \cdot B(2) - A(2) \cdot B(1),$$

$$(6.1)$$

where $A(1)$, for example, means the wave function for hydrogen atom A, written for the coordinates of electron No. 1.

Suppose for the moment that these functions do approximate two possible

electronic wave functions for the hydrogen molecule. Then some of the physical differences between them can be examined by looking at their squares, which will measure the probability that electron No. 1 is in the region around x_1, y_1, z_1, and electron No. 2 is in the region around x_2, y_2, z_2. For example, as Discussion 6.3 (see page 45) shows, the probability that the two electrons are both midway between the protons, in their strongest bonding positions, is finite when they are in the state described by ψ_{sym} and increases with decreasing separation of the protons. On the other other hand the wave function ψ_{anti} vanishes for that position of the electrons. When this kind of job is done throughout the space around the pro-

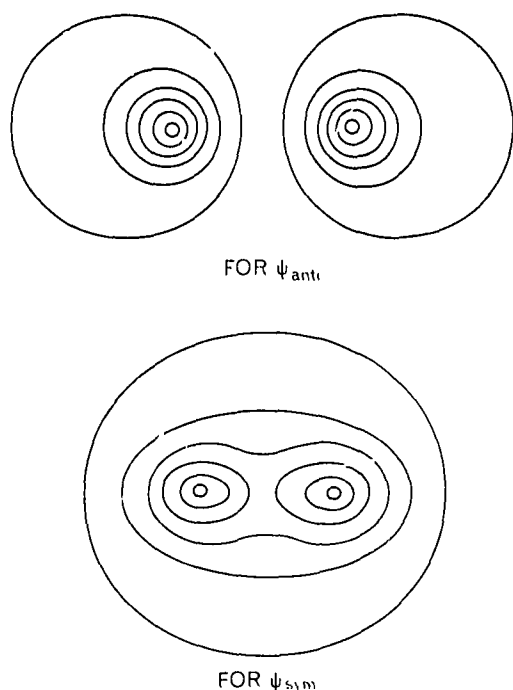FOR ψ_{anti}

FOR ψ_{sym}

Fig. 6.6 Contours of equal electron density, in a plane containing the two nuclei, for the spacially antisymmetric and the spacially symmetric wave function for the hydrogen molecule in the approximation of Eq. (6.1).

tons, the contours of equal electron density turn out to look like Fig. 6.6.

Thus it seems possible, from Fig. 6.6, that ψ_{sym} will be a state that bonds the two protons by piling up negative charge between them. Looking back at the expression for probability density in Discussion 6.3, you see why this piling up takes place. The first two terms in that expression are merely the terms coming from the two separate atoms. The last term appears because the electrons can exchange places: it is an exchange term. Clearly this term has its largest absolute value where the 1s wave function for the two atoms overlap. In the case of ψ_{sym} this term brings more electron density into that region than the overlapping of the atoms would provide by way of the first two terms. In the case of ψ_{anti} the overlap tends to push electron density away from the overlapping region - again more than

the mutual repulsion of the electrons would accomplish by itself.

Notice that this effect is a result of a very general feature of wave mechanics. A state made up by adding together two component states will not usually have properties that are simply the sums of the corresponding properties of those two component states. That is because observable properties of a state all depend on the square of the wave function, in one guise or another. The expression in Discussion 6.3 for the probability density shows the result of this clearly in its last term, for the first two terms are simply the squares of the wave functions for the component states.

Now of course the validity of these trial functions still swims in a sea of physical intuition. The functions ψ_{sym} and ψ_{anti} are certainly not exact solutions of Schroedinger's equation for the hydrogen molecule, and nothing up to this point has shown whether they are good or bad approximations. The only way to find out is to calculate some observable properties with the aid of these wave functions and check the calculated values against experimental results.

The most important single property to calculate is the energy as a function of the separation of the protons - the $E(R)$ discussed in the last chapter. Then you can see whether the sum of $E(R)$ and the repulsive energy of the two protons goes through a minimum at some value of R. Using the reasoning of the last chapter, you would check that value R_0 against the known interatomic distance in the hydrogen molecule, and the corresponding energy U_0 against the known binding energy of the molecule.

It turns out that the check, carried out in the appendix to this chapter, gives a very satisfying answer. Such a check does not rigorously show whether the wave functions themselves are good approximations, but only whether they are capable of yielding good approximations to the

Discussion 6.3

·DISTRIBUTION OF ELECTRONS

The squares of the wave functions given by the expressions (6.1) are

$$\psi^2 = A^2(1) \cdot B^2(2) + A^2(2) \cdot B^2(1)$$
$$\pm 2\, A(1) \cdot B(2) \cdot A(2) \cdot B(1),$$

where + applies to ψ_{sym} and − applies to ψ_{anti}. In order to examine the prediction that this makes along the line connecting the two protons, substitute the values of the atomic wave functions shown in Discussion 6.2, and let $x_1 = y_1 = x_2 = y_2 = 0$. Then

$$\psi^2_{line} = \exp -2[\,|z_1 - R/2| + |z_2 + R/2|\,]$$
$$+ \exp -2[\,|x_2 - R/2| + |z_1 + R/2|\,]$$
$$\pm 2\exp -[\,|z_1 - R/2| + |z_2 - R/2|$$
$$+ |z_1 + R/2| + |z_2 + R/2|\,].$$

At the middle of the line between the two protons $z_1 = z_2 = 0$. Substituting these values of the z's in the preceding expression shows that the probability that the two electrons are both midway between the protons, in their strongest bonding positions, is proportional:

for ψ_{sym} to $4e^{-2R}$,

for ψ_{anti} to 0.

energy. Some additional faith in the form of the wave functions, however, comes from the physically sensible reasoning used in constructing them.

It is convenient to have a word for the space-dependent part of a wave function for one electron, to distinguish it from the whole wave function which includes reference to the spin. "Orbital" is the customary word. Such a function as the 1s wave function, obtained by solving Schroedinger's equation for an atom, is called an "atomic orbital." Such functions as the wave functions used in the last chapter for the hydrogen molecule-ion are called "molecular orbitals." The foregoing method of approximation in a many-electron problem is therefore often called the "atomic orbital method."

Look now at the other way of picturing the hydrogen molecule - a "molecular orbital method," in which the orbitals for the hydrogen molecule-ion are filled with two electrons in succession. As the last chapter remarked, Schroedinger's equation can be solved for an electron in the presence of two protons separated by the distance R, but the solutions cannot be expressed in closed form in terms of tabulated functions. Of the two solutions corresponding to the lowest energies in the interesting region of R, one is spacially symmetric, the other antisymmetric, with respect to the perpendicular plane bisecting the line between the two protons. Fig. 6.7 shows roughly the character of the
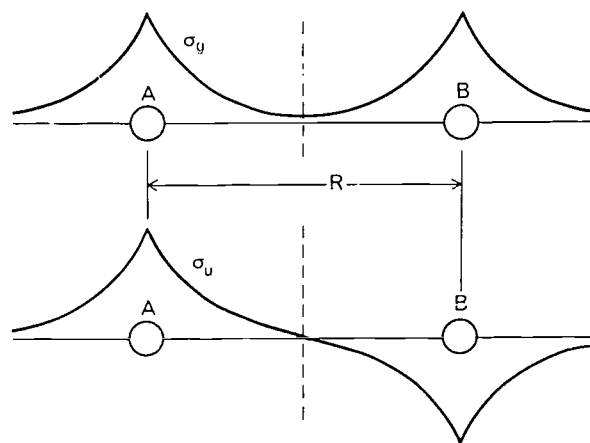

Fig. 6.7 The general form of cross-sections of the spacially symmetric ("gerade") and spacially antisymmetric ("ungerade") wave functions for the hydrogen molecule.

1	$\sigma_g(1) \cdot \sigma_g(2)$	SPINS OPPOSITE
2	$\sigma_u(1) \cdot \sigma_u(2)$	SPINS OPPOSITE
3	$\sigma_g(1) \cdot \sigma_u(2) + \sigma_u(1) \cdot \sigma_g(2)$	SPINS OPPOSITE
4	$\sigma_g(1) \cdot \sigma_u(2) - \sigma_u(1) \cdot \sigma_g(2)$	SPINS PARALLEL

Table 6.1

1	$[A(1) + B(1)] \cdot [A(2) + B(2)]$
2	$[A(1) - B(1)] \cdot [A(2) - B(2)]$
3	$[A(1) + B(1)] \cdot [A(2) - B(2)]$ $+ [A(1) - B(1)] \cdot [A(2) + B(2)]$
4	$[A(1) + B(1)] \cdot [A(2) - B(2)]$ $- [A(1) - B(1)] \cdot [A(2) + B(2)]$

Table 6.2

1	$A(1) \cdot A(2) + B(1) \cdot B(2) + \psi_{sym}$
2	$A(1) \cdot A(2) + B(1) \cdot B(2) - \psi_{sym}$
3	$2[A(1) \cdot A(2) - B(1) \cdot B(2)]$
4	$-2\psi_{anti}$

Table 6.3

wave functions along the line of the protons.

Now consider the ways in which two electrons can occupy these molecular orbitals. To follow convention, call the spacially symmetric orbital σ_g (g = "gerade" = "even") and the spacially antisymmetric orbital

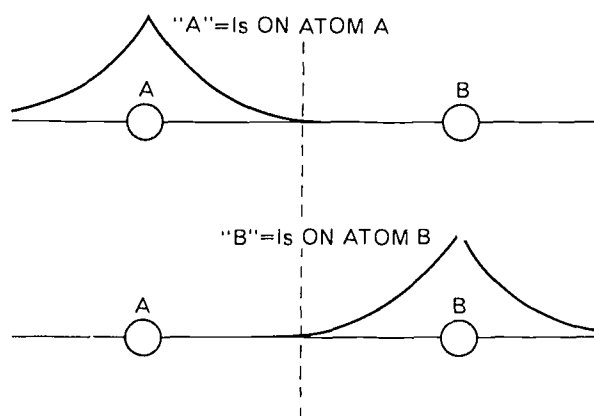"A"=1s ON ATOM A

"B"=1s ON ATOM B

Fig. 6.8 Cross sections of the atomic 1s wave functions on two hydrogen atoms, whose sum and differe.ce approximate the two molecular wave functions of Fig. 6.7.

σ_u (u = "ungerade" = "odd"). The two electrons will obey the exclusion principle if they are in any of the wave functions shown in Table 6.1.

The question now arises, why does the molecular orbital method afford four possibilities, three with spins paired, whereas the atomic orbital method seemed to yield only two possibilities, one with spins paired? The answer comes from looking at a way of approximating σ_g and σ_u in terms of "A" and "B": the 1s wave functions on the two atoms, which you used before. This way of approximating molecular orbitals is often called the "LCAO approximation": the linear combination of atomic orbitals. Fig. 6.8 shows cross sections of A and B. Clearly A + B looks like σ_g (Figure 6.7) and A — B looks like σ_u. By using these approximations, the four functions of Table 6.1 can be rewritten into the forms shown in Table 6.2. When the products in Table 6.2 are expanded, and the results are compared with Eq. (6.1), the four functions take the forms shown in Table 6.3.

These forms now call attention to two combinations of the atomic orbitals that were neglected in the earlier pursuit of the atomic orbital method: the combinations $A(1) \cdot A(2)$ and $B(1) \cdot B(2)$. Clearly the states that these combinations represent are those in which both electrons with spins paired, are on one or the other proton: the "ionic states" H^-H^+ and H^+H^- (Fig. 6.9). It is altogether probable that an approximation to the true wave function for the hydrogen molecule would be better if it included a little of these combinations along with ψ_{sym}. They cannot be used with ψ_{anti} because in the ionic combinations the spins are antiparallel, and in ψ_{anti} the spins are parallel.

The way to effect this improvement in the approximation is to add to ψ_{sym} proportions C_A of $A(1) \cdot A(2)$ and C_B of $B(1) \cdot B(2)$. For the hydrogen molecule, whose two atoms are identical, you can take $C_A = C_B \equiv C$. When the bonded atoms differ, C_A may not

equal C_B, and their inequality will
betoken a mixture of ionic and coval-
ent bonding. In order to determine the
best value of C, you can use the fact
that the molecule will surely choose
that value that gives it the lowest
energy.[22]

Alternatively, a similar proce-
dure could be followed with the first
three molecular orbitals in Table 6.1.
Either procedure will lead finally to
two molecular states, constructed
either from the two atomic orbitals
A and B or the two molecular orbitals
σ_g and σ_u. In one of these states, a
bonding state, the spins of the elec-
trons will be opposed, and the energy
will pass through a minimum as R var-
ies. In the other state, an antibond-
ing state, the spins will be parallel,
and the state will repel the protons
at all values of R. This sort of analy-
sis has been applied to other atoms
as well as hydrogen, and its results
can be summarized in a few useful gen-
eralizations.

In the first place, when molecu-
lar orbitals are made by taking
"linear combinations of atomic orbi-
tals," the number of finally independ-
ent molecular orbitals is always the
same as the number of atomic orbitals
employed. In the example of this chap-
ter, the number is two. Usually half
the molecular orbitals are bonding
orbitals and half are antibonding.
Since each orbital will hold only two
electrons, the number of electrons
involved in bonding will not exceed
the number of atomic orbitals that
have been invoked. When these numbers
are equal, the molecule shows "satur-
ated valency" on the part of all its
atoms. When there are fewer electrons
available for bonding than the number
of atomic orbitals involved in the
bonding, the bonds are called "elec-
tron-deficient bonds." The metallic
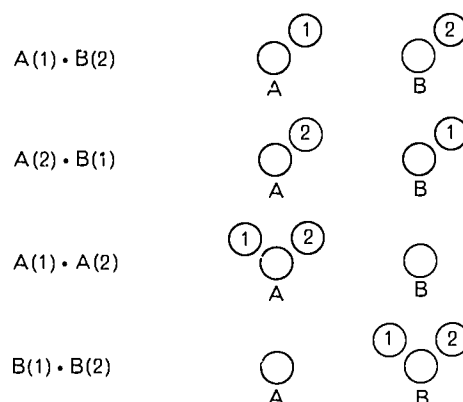bond in particular can be regarded as
an electron-deficient bond.

Fig. 6.9 Four combinations of atomic
states that can contribute to the bonding
of two atoms by a pair of electrons. The
upper two are those used in the approxima-
tions of Eq. (6.1); the lower two are
"ionic' or "polar" states.

Usually the bonding orbitals
that lie lowest in the energy scale
are orbitals for states in which the
spins are opposed. Most of the mole-
cules in nature are bonded by pairs
of electrons with opposed spins; but
there are exceptions, of which mole-
cular oxygen is the most familiar. In
oxygen two of the four bonding elec-
trons have parallel spins because
there is an "orbital degeneracy"; two
bonding orbitals have the same energy.
Of the resulting bonding states, one
is a state with spins opposed, the
other with spins parallel.

Most importantly, however, the
analysis reemphasizes the picture of
bonding as an accumulation of nega-
tive charge between the positive nu-
clei - the picture already presented
in the last chapter. You can see two
opposing tendencies at work. The
electrons tend to push each other
away. But this is outweighed by the
fact that the potential energy of all
of them is lowest when they are be-
tween the nuclei. They would all rush
there, and everything would form bonds
with everything else, were it not for
the behavior described by the exclu-
sion principle. In accordance with
that principle they find states that
are antisymmetric to their interchange.

[22]This idea can be embodied in a calculation by
using the variational method described in Wave-
Mechanical Properties of Stationary States.

As in atoms, so in molecules, that law of antisymmetry limits the occupancy of each orbital. Only some of the states will give electron densities favorable for bonding.

The bonding states, having energy minima with respect to variations of the nuclear arrangement, are those that permit the electronic charge to accumulate between the nuclei. When those bonding states are viewed as constructed out of atomic orbitals, the accumulation of charge is greatest where the atomic orbitals would overlap the most. And the accumulation is greater than that overlap alone would provide, in consequence of an exchange effect that augments the simple sum.

Appendix   BINDING ENERGY OF HYDROGEN BY THE METHOD OF ATOMIC ORBITALS

The expectation value of the true energy[23] will be $E(R) = \int \psi H \psi d\tau$, where H is the Hamiltonian operator used in Schroedinger's equation for the true case (Discussion 6.2) and ψ is the true wave function, properly normalized. The same method can be used here to calculate approximate energies, by employing the true Hamiltonian and the approximate wave functions ψ_{sym} and ψ_{anti} (Eqs. 6.1), taking care of normalization by dividing by $\int \psi^2 d\tau$:

$$E(R) = \frac{\int \psi H \psi d\tau}{\int \psi^2 d\tau}. \qquad (A6.1)$$

Look first at the normalization integral in the denominator: it is the integral, over all the coordinates, of the expression in Discussion 6.3. Its first two terms are

$$\int A^2(1)d\tau_1 \cdot \int B^2(2)d\tau_2$$
$$+ \int A^2(2)d\tau_2 \cdot \int B^2(1)d\tau_1.$$

If A(1) etc. are chosen as the normalized solutions to the hydrogen-atom problem, each integral equals unity by the definition of normalization. The last term breaks into the product

$$\pm 2\int A(1) \cdot B(1)d\tau_1 \cdot \int A(2) \cdot B(2)d\tau_2.$$

Since both the integrals in this product have the same mathematical form,

the product is a square, and therefore essentially positive. Often denoted by S, it has the value

$$S = e^{-2R}\left(1 + R + \frac{1}{3}R^2\right)^2. \qquad (A6.2)$$

Thus the denominator is

$$\int \psi^2 d\tau = 2(1 \pm S). \qquad (A6.3)$$

The integral in the numerator can be broken up also. From the first two equations of Discussion 6.2,

$$H = H_{AB} - \frac{1}{r_{1B}} - \frac{1}{r_{2A}} + \frac{1}{r_{12}}$$
$$= H_{BA} - \frac{1}{r_{1A}} - \frac{1}{r_{2B}} + \frac{1}{r_{12}}. \qquad (A6.4)$$

Since each of the two parts of the approximate solutions is a solution to one of those equations,

$$H_{AB}[A(1) \cdot B(2)] = 2E_H[A(1) \cdot B(2)],$$
$$H_{BA}[A(2) \cdot B(1)] = 2E_H[A(2) \cdot B(1)].$$
$$(A6.5)$$

By the use o (A6.4) and (A6.5) the integrand in the numerator of Eq. (A6.1) becomes

$$\psi H \psi = [A(1) \cdot B(2) \pm A(2) \cdot B(1)]$$
$$\cdot \left\{2E_H[A(1) \cdot B(2) \pm A(2) \cdot B(1)]\right.$$
$$+ \left(\frac{1}{r_{12}} - \frac{1}{r_{1B}} - \frac{1}{r_{2A}}\right)A(1) \cdot B(2)$$

[23] The calculation of wave-mechanical expectation values is described in _Wave-Mechanical Properties of Stationary States_, a monograph in this series.

$$\pm \left(\frac{1}{r_{12}} - \frac{1}{r_{1A}} - \frac{1}{r_{2B}}\right) A(2) \cdot B(1)\}$$

$$= 4E_H(1 \div s) + \left(\frac{1}{r_{12}} - \frac{1}{r_{1B}} - \frac{1}{r_{2A}}\right) A^2(1) \cdot B^2(2)$$

$$+ \left(\frac{1}{r_{12}} - \frac{1}{r_{1A}} - \frac{1}{r_{2B}}\right) A^2(2) \cdot B^2(1)$$

$$\pm \left[\left(\frac{1}{r_{12}} - \frac{1}{r_{1B}} - \frac{1}{r_{2A}}\right) + \left(\frac{1}{r_{12}} - \frac{1}{r_{2A}} - \frac{1}{r_{1B}}\right)\right]$$

$$A(1) \cdot B(2) \cdot A(2) \cdot B(1).$$

(A6.6)

The terms in the integral of the expression (A6.6) can again be identified as equivalent in pairs because they have the same mathematical form: they merely have the labels 1 and 2 interchanged on their variables of integration. The integral can therefore be written in the form

$$\int \psi \bar{H}\psi \, d\tau = 4E_H(1 \pm S) + 2(I_1 \pm I_2),$$
(A6.7)

where

$$I_1 = \int\int \left(\frac{1}{r_{12}} - \frac{1}{r_{1A}} - \frac{1}{r_{2B}}\right) A^2(2) \cdot B^2(1) d\tau,$$
(A6.8)

and

$$I_2 = \int\int \left(\frac{\cdot}{r_{12}} - \frac{1}{r_{1A}} - \frac{1}{r_{2B}}\right) A(1) \cdot B(1)$$

$$\cdot A(2) \cdot B(2) d\tau.$$

(A6.9)

Hence finally

$$E(R) = 2E_H + \frac{I_1 \pm I_2}{I \pm S}, \qquad (A6.10)$$

where + applies to the state ψ_{sym} and − applies to the state ψ_{anti}.

The integral I_1 is easily eval uated, but the integral I_2 is not. Instead of going into mathematical detail, accept the results shown graph-

ically in Fig. 6.10. By adding to them the repulsive energy e^2/R of the two protons, Fig. 6.11 can be drawn for the energy $U(R)$ of the molecule. The values of R_0 and U_{min} obtained for the molecule in the state ψ_{sym} are 0.8 Å, and −3.16 eV, to be compared with the experimental values of 0.74 Å and −4.75 eV.

In comparing the value of $U_{min} = -4.74$ eV with the value of $U_o = -31.7$ eV cited at the end of the last chapter, notice that U_o refers to a zero of energy in which the molecule is entirely dispersed into protons and electrons that are all far from one another, whereas U_{min} refers
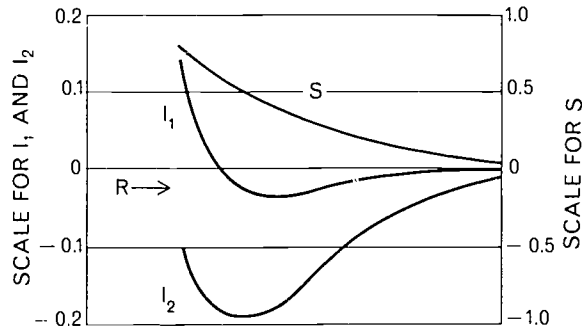

Fig. 6.10   Integrals, as functions of internuclear separation, for an approximation to the electronic part of the binding energy of the hydrogen molecule.
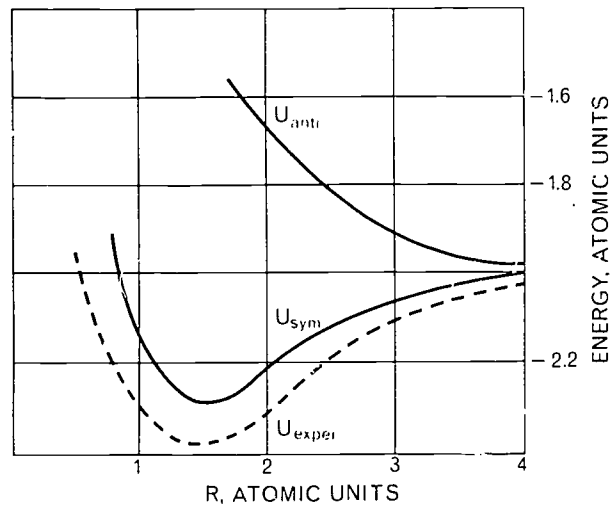

Fig. 6.11   Total energy $(E(R) + e^2/R)$ of the hydrogen molecule, calculated by the method of approximation embodied in Eqs. (6.1).

to a zero of energy in which two hy-
drogen atoms are separated. Hence the
difference corresponds to twice the
ionization potential of hydrogen:
2×13.5 eV·U_{min} is called the dis-
sociation energy of the molecule.

Figures 6.10 and 6.11 show that
the major contribution to the differ-
ence between the energies of the sym-
metric and antisymmetric states of the
molecule, in the interesting region
of R, has come from the integral I_2.
Equation (A6.9) shows that this inte-
gral contains the combination of the
component one-electron wave functions
that was found responsible for piling

up or pushing away the electron den-
sity between the protons (Discussion
6.3). This integral is called the "ex-
change integral." The fact that it is
negative makes the state ψ_{sym}, with
the spins of the two electrons anti-
parallel or "paired," the state with
the lower energy. Since that state
shows a minimum as R varies, it is
able to provide a bond between the
protons: it is a "bonding state" of
the molecule. The other state, which
is repulsive for all values of R, and
in which the two spins are parallel,
is an "antibonding state."

The discussion of the last chapter has constructed a picture of covalent bonding that can be codified for many purposes into the following rules. A covalent bond forms when (1) the atomic orbitals of two atoms overlap, (2) an electron in each atom can exchange with an electron in its partner atom without violating the exclusion principle, and (3) the resulting exchange leads to an increased electronic density between the atoms. And that last condition is usually fulfilled only when the two exchanging electrons have opposite spins.

Examine a schematic way of studying the operation of these rules in Fig. 7.1, where the electrons and their spins - up and down - are numbered and shown by arrows associated with symbols for the atoms whose bonding is in question. For example, in the attempt of the helium atom, with two 1s electrons, to form a bond with the hydrogen atom with one 1s electron (Fig. 7.1a), two alternative exchanges among the three electrons can be visualized. If No. 1 exchanges with No. 3, the helium atom will have No. 2 and No. 3 in the same atomic orbital, which the exclusion principle forbids because their spins are the same. On the other hand, if No. 2 exchanges with No. 3, the exchange will be antibonding because the exchanging spins are the same. Hence no HeH molecule is to be expected, and in fact that species has not been found in nature. Similarly, of the possible exchanges between the two helium atoms (Fig. 7.1b), the exchanges of No. 1 and No. 4, and of No. 2 and No. 3, would violate the exclusion principle, and the exchanges of No. 1 and No. 3, and of No. 2 and No. 4, would be antibonding.

Notice as you go that the only behavior of these electrons not prohibited by the exclusion principle finds them in antibonding orbitals.

The last chapter showed (Fig. 6.6) that in such an orbital electron density is pushed away from the space between the nuclei, and also (Fig. 6.11) that the electronic energy increases rapidly as the distance between the nuclei shortens. Here is the principal origin of the repulsive force between atoms. When the atoms approach each other they bounce away, as if they were balls that are only slightly compressible, because their electrons are forced into antibonding orbitals.

In order to extend the reasoning, begun with hydrogen and helium, to atoms that contain more than two electrons, recall the ways in which electrons occupy the one-electron states that an atom presents. In building up the periodic table of the elements by the aufbauprinzip, each successive atom receives one more electron, whose negative charge is compensated by an increased positive charge on the nucleus. That electron enters the state of lowest energy not already fully occupied. According to
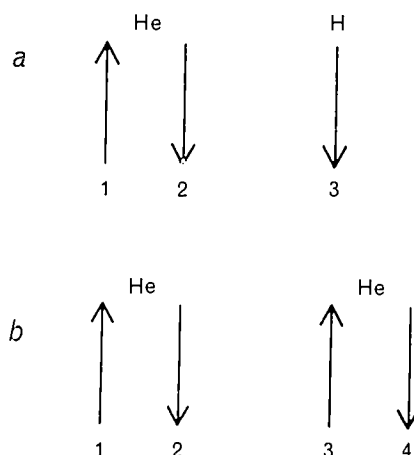

Fig. 7.1 A helium atom does not form a covalent bond with a hydrogen atom (a), or with another helium atom (b).

51

the exclusion principle each state is
fully occupied when it has been adop-
ted by two electrons, and then those
electrons necessarily have opposed
spins. The relative energies of the
one-electron states can be qualita-
tively shown in a diagram like Fig.
7.2, where boxes symbolize the states,
and their relative energies are sug-
gested by the height at which the
boxes appear.

For the first ten elements in the
periodic table the occupancies of
these atomic states are shown in Fig.
7.3. Each occupying electron is repre-
sented by an arrow, and the fact that
the spins of two electrons in the same
one-electron state are opposed is sym-
bolized by directing the arrows oppo-
sitely. In general only the electrons
in the occupied states of highest en-
ergy will participate in bonding;
electrons in states of lower energy
are too tightly bound within their
parent atom to visit another. When
atoms are pulled toward one another
by bonding forces of any sort, the
electrons that completely occupy the
states of lower energy in them are
forced into antibonding orbitals and
so hold the atoms apart, giving to
each atom an effective size and to
each bond an effective length.

Such diagrams as those in Fig.
7.3 can now be used to symbolize how
the proposed rules for covalent bond-
ing operate with the higher-energy
electrons in these atoms. The oxygen
atom has two 1s electrons, two 2s
electrons, and four 2p electrons, of
which the last six are shown in Fig.
7.4a. In forming the water molecule,
H_2O, each hydrogen atom exchanges its
electron with one of the 2p electrons
in the oxygen atom. In the ammonia
molecule, NH_3 (Fig. **7.4b**), three hy-
drogen atoms exchange an electron in
a similar way with a nitrogen atom.
Figure **7.4c** diagrams the diatomic
fluorine molecule according to the
present scheme.

The single electron in a hydrogen
atom is in a state that has spherical
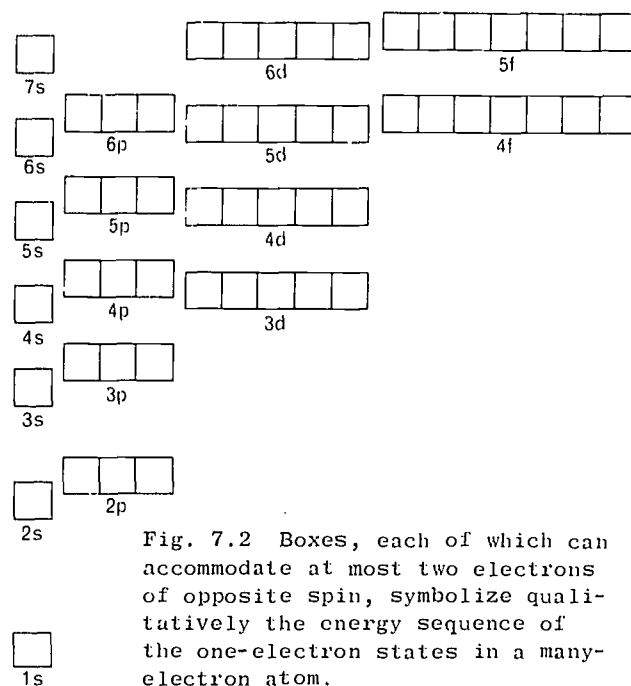symmetry about the proton. But the

Fig. 7.2 Boxes, each of which can
accommodate at most two electrons
of opposite spin, symbolize quali-
tatively the energy sequence of
the one-electron states in a many-
electron atom.

electrons in the oxygen atom and the
nitrogen atom that participate in the
bonding formalized in Fig. **7.4** are in
p states, which are not spherically
symmetrical. In any one such atom the
different p states give electronic
densities whose maxima project in dif-
ferent directions, as Fig. **7.5** shows.
Hence if covalent bonding is strongest
when the wave functions of the parti-
cipating atoms can overlap the most,
as the last chapter suggested, one
would expect to find that the angles
between the bonds to the several hy-
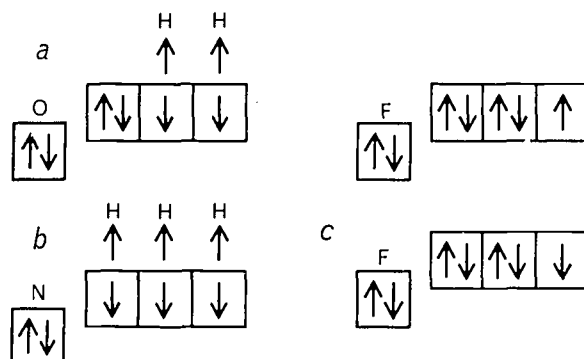drogen atoms in water and ammonia

Fig. 7.4 The exchanges which make possible
the bonds in (a) H_2O, (b) NH_3, and (c) F_2.

Fig. 7.3 Electron configurations in the ground states of atoms of the first ten elements in the periodic table, diagramed by the method of Fig. 7.2.

would correspond with the angles between the maxima in Fig. 7.5, as shown in Fig. 7.6 (see next page).

The experimentally determined angles are actually not $90°$, but $105°$ in water and $109°$ in ammonia. The differences are probably due to the fact that the bonds are not purely covalent but are partly ionic. The last chapter showed that the states H^+H^- and H^-H^+ might contribute appreciably to the completed atomic-orbital picture of the hydrogen molecule. When the two bonded atoms are not of the same species, the two ionic states will usually not contribute equally. Which one will predominate depends on atomic details of participating atoms summarized as their "relative electronegativity." In the cases of water and ammonia, there are appreciable contributions from ionic states of the type H^+O^-H and HO^-H^+, diagramed in Fig. 7.7 (see next page). Hence the hydrogen atoms tend to repel one another, and the configuration of lowest energy shows a larger bond angle than the p bond angle.

This idea can be checked by comparing the measured bond angles and dipole moments of water (H_2O) and hy-

appropriate when there are 3 perpendicular axes (e.g. NH_3)

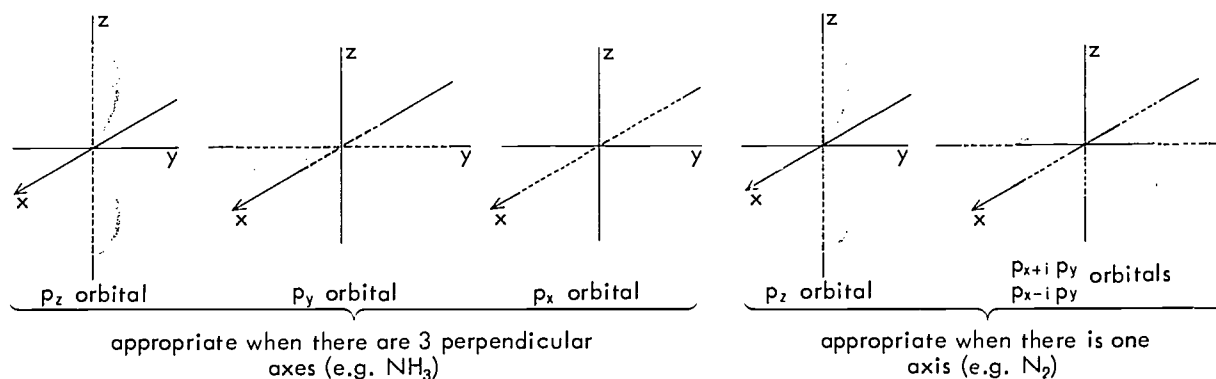appropriate when there is one axis (e.g. N_2)

Fig. 7.5 The angular dependence of the squares of the p orbitals. These multiply the squares of the radial dependences to yield the squares of the orbitals.
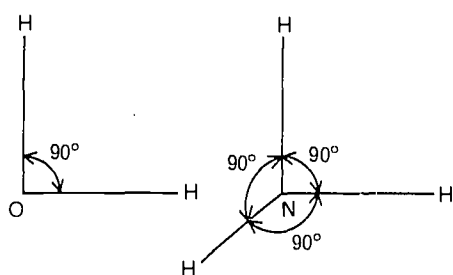
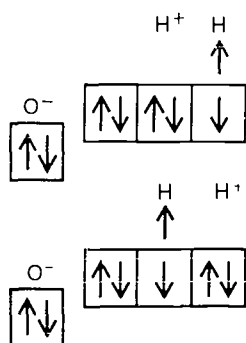Fig. 7.6   The bond angles in H_2O and NH_3 that Fig. 7.5 would suggest.

Fig. 7.7   The ionic contributions to the bonding in H_2O.

MOMENT ANGLE	BOND ANGLE	DIPOLE MOMENT $\times 10^{18}$ esu
H_2O	105°	1.84
H_2S	92°	0.93
NH_3	109°	1.46
PH_3	93°	0.55

Fig. 7.8   Evidence that the departure of actual bond angles from those which Fig. 7.5 would suggest is caused by ionic contributions to the bonding.
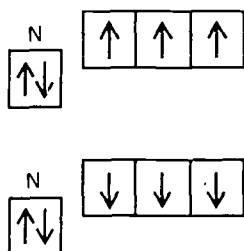

Fig. 7.9   The exchanges in the triply bonded nitrogen molecule.

drogen sulfide (H_2S), and of ammonia (NH_3) and phosphine (PH_3), tabulated in Fig. 7.8. Here sulfur and phosphorus are also bonding by electrons that are in atomic p orbitals. But from other evidence sulfur and phosphorus are known to be less electronegative than oxygen and nitrogen.

Look now at the character of the bonds between two atoms that are exchanging more than one pair of electrons. The nitrogen molecule, for example, consists of two nitrogen atoms, and the exchanges could be schematized as in Fig. 7.9. As Fig. 7.5 shows, the three 2p atomic orbitals of the two atoms cannot all overlap to their maximum. The line between the two atoms establishes a z axis; one can expect that the p_z orbitals will be directed along that line and will exhibit maximum overlap, and the p_x and p_y orbitals, directed at right angles to z, will overlap less. Bonds formed by the overlapping of atomic s orbitals, and of atomic p orbitals directed along the line of the bond, are often called σ bonds; and bonds formed by the overlapping of p orbitals that are directed at right angles to the bond are called π bonds.

At first glance one would expect that the triple bond in nitrogen would be stronger than a single bond, but not three times as strong. Actually the multiplicity of the bond tends to strengthen each of its components somewhat. The increased number of components to the bond pulls the atoms closer together; and by thus increasing the overlap in each component, it increases the strength of each. Table 7.1 shows how this effect is reflected in the measured properties of the diatomic molecules formed by the atoms in the first period of the periodic table.

In showing boron and carbon as having valencies of one and two, and beryllium as zero-valent like the rare gases, Table 7.1 accurately reflects their behavior in these diatomic molecules but in almost no other chemical respect. The normal valencies of beryllium, boron, and carbon are two,

	Li–Li	B–B	C = C	N ≡ N	O = O	F–F
INTERATOMIC DISTANCE (ANGSTROMS)	2.67		1.31	1.09	1.21	1.45
DISSOCIATION ENERGY (ELECTRON VOLTS PER MOLECULE)	1.13	3.00	3.61	9.78	5.09	3.13

Table 7.1 Properties of Diatomic Molecules.

three and four respectively, as their positions in the periodic table suggest. The reason for their higher valency lies in the relatively low energy required to excite one of their 2s electrons to a 2p state. If the energy gained by forming additional bonds more than compensates for the excitation energy, the atom will form those bonds. Thus the fact that the two outermost electrons in beryllium completely fill the 2s orbital does not exclude bonding, as does the filling of the 1s state in helium. The energy required to excite one electron from the 2s to the 2p orbital in beryllium is only 2.7 eV, whereas the energy required to excite one of the 1s electrons of helium to the 2s orbital is 10 eV. For most bonding purposes, therefore, the states of beryllium, boron, and carbon can be imagined to be the excited states schematized in Fig. 7.10.

An interesting problem now arises in examining the bonds formed by carbon. According to the scheme of the excited state shown in Fig. 7.10, carbon should form single bonds of two sorts, one bond using its 2s orbital and three using its 2p orbitals. In fact, however, methane (CH_4) and other such molecules have properties that can be explained only by supposing that all four hydrogens are bonded in the same way, with the same strength, at tetrahedral angles. This fact can best be explained by the hypothesis that hybrid orbitals are formed from combinations of the s and p orbitals, as described in Discussion 7.1 (see next page).

The angular dependence of any one of these orbitals is shown in cross section in Figure 7.11; they differ only in the direction of maximum density. The four directions are those from the center toward the four cor-
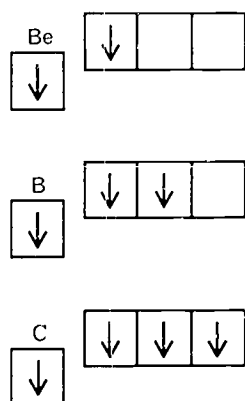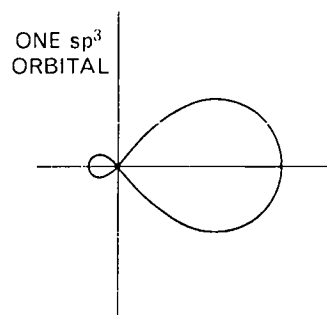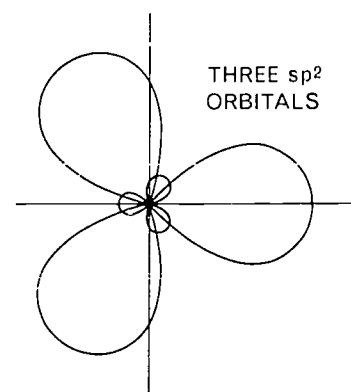

Fig. 7.10. Readily excited states of the beryllium, boron, and carbon atoms account for their valencies.

Fig. 7.11 Cross section of the angular factor in one of the four sp^3 hybrid orbitals directed toward the corners of a tetrahedron.

Fig. 7.12 Cross section of the squares of the three sp^2 hybrid orbitals, directed at 120° to one another in the plane of the paper.

Discussion 7.1

sp^3 HYBRIDIZATION

In the formation of hybrid orbitals it is assumed that the proximity of other atoms so modifies the character of the one 2s and the three 2p orbitals of an atom that their energies are sufficiently close to make them degenerate (see <u>Wave-Mechanical Properties of Stationary States</u>). Then any linear combination of them is also a possible orbital. In particular, you can make the combinations

$$\psi_1 = \tfrac{1}{2}(s + p_x + p_y + p_z),$$
$$\psi_2 = \tfrac{1}{2}(s - p_x - p_y + p_z),$$
$$\psi_3 = \tfrac{1}{2}(s - p_x + p_y - p_z),$$

$$\psi_4 = \tfrac{1}{2}(s + p_x - p_y - p_z).$$

The constituent atomic orbitals are orthogonal; and if they are also normalized, these hybrid orbitals can be seen to be normal and orthogonal by forming their squares and products. Since the s function is spherically symmetrical, and since the angular dependence of p_x, p_y, and p_z is proportional to x/r, y/r, and z/r, respectively, the four sp^3 hybrids can be seen to have their maxima directed respectively toward the four corners of a tetrahedron centered at the origin of coordinates.

ners of a regular tetrahedron, and each is cylindrically symmetrical about its direction. The bonds formed by these orbitals are called <u>sp^3 hybrids</u>.

Carbon can also form double bonds, and here a different hybridization ap-

pears. Only two of the p orbitals are combined with the s orbital, in a way that produces three orbitals whose maximum densities are directed at 120° to one another in the (x,y) plane. Figure 7.12 (see preceding page) shows in cross section the angular dependence of
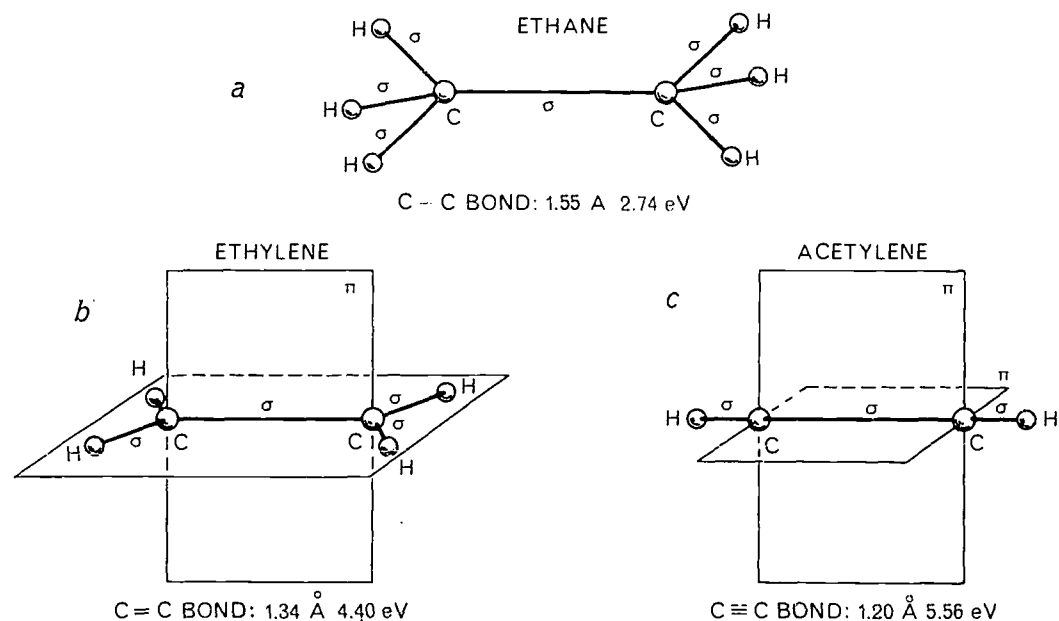

ETHANE

C – C BOND: 1.55 Å 2.74 eV

ETHYLENE

C = C BOND: 1.34 Å 4.40 eV

ACETYLENE

C ≡ C BOND: 1.20 Å 5.56 eV

Fig. 7.13 The σ and π bonds in (a) ethane (H_3C-CH_3), (b) ethylene ($H_2C=CH_2$), and (c) acetylene (HC≡CH) molecules. The planes marked π are the planes determined by the axes of the p-orbitals in the atoms that overlap to form a bond.

their electron density. The double bond then consists of one σ bond, formed by one of these <u>sp^2 orbitals</u> and a π bond formed by the remaining p_z orbital, whose maximum density is perpendicular to the plane of the sp^2 bonds.

Finally, carbon can form a triple bond. Here two orbitals, in opposite directions along the z axis, are formed by hybridizing the s and p_z orbitals. One of the hybrid orbitals forms the σ bond and the p_x and p_y orbitals form the two π bonds, in much the same way that the three p orbitals of nitrogen form the triple bond in the nitrogen molecule. The remaining <u>sp orbital</u> forms a σ bond to another atom, to saturate the valency of carbon.

Figure 7.13 shows examples of the three bonding schemes in ethane (H_3C-CH_3), ethylene (H_2C=CH_2), and acetylene (HC≡CH), in schematic form. Notice an interesting result of the double bond in ethylene; the hydrogen atoms are constrained to lie in the same plane, perpendicular to the plane of the π bond. Molecular spectroscopy shows that in fact ethylene has a high torsional stiffness. In ethane the only interference with the free rotation of one CH_3 group relative to the other about their common axis is caused by the slight repulsive forces between the hydrogen atoms.

In these ways the pictures used by chemists for nearly a century, in which covalent bonds are analogized to sticks projecting from holes in the bonded atoms, are remarkably well justified. Like sticks, the bonds have determinable lengths. Like sticks, they project from the atoms at determinable angles. A single bond permits groups of atoms to rotate fairly freely about it. much as a stick would permit them. And atoms that are connected by several bonds are restrained from rotating about them, much as sticks would restrain them.

PROBLEMS

7.1 From the most recent calculations, it appears probable that the helium hydride ion (HeH)$^+$ is a stable species with dissociation energy between 1.75 and 2.05 eV. Use the method of the discussion at the beginning of this chapter to show why this ion might be a stable species whereas the neutral HeH molecule would not.

7.2 (a) Picture the bonding in the BeO molecule by a diagram like Fig. 7.2(c) and Fig. 7.7, on the assumption that the bond is purely covalent.

(b) Using the argument that atoms in molecules attempt to adopt the electronic configurations of the rare gases, do you expect to find an important ionic ingredient in the BeO bond, and if so, in which direction will the dipole moment point?

7.3 (a) Picture the bonding in the carbon dioxide molecule in the manner of problem 7.2(a).

(b) Since the CO_2 molecule is in fact linear, picture the bonding in the manner of Fig. 7.11, on the assumption that the carbon atom bonds each oxygen atom by a σ bond which is an sp_z hybrid and by a π bond which is a p_x orbital for one oxygen atom and a p_y orbital for the other.

7.4 From the considerations in problems 7.2 and 7.3, give a reason why at ordinary temperatures carbon dioxide is a gas and beryllium oxide is a solid.

The discussions of ionic bonding forces in Chapter 3 and of dispersion forces in Chapter 4 pointed out that those forces can form bonds between indefinite numbers of atoms. They are indiscriminate in their operation and find their only limitation in the fact that the sizes of atoms limit the number that can cluster about any one atom. Since those forces all fall off with increasing distance, their bonds are strongest between nearest neighbors.

On the other hand, the discussion of covalent bonds in the last three chapters has emphasized the bonding of atoms in pairs. The covalent bonding of more than two atoms into a polyatomic molecule has been pictured as occurring by the formation of links between adjacent atoms, each welded by the localized behavior of electrons that remain associated with no more than two atoms.

For most molecules this is a useful habit of thought. As the last chapter has shown, it provides a way of thinking that can give a good account of many of the facts of chemistry. The structural diagrams drawn by chemists formalize this way of thinking, and organic chemistry has profited from it especially. By such diagrams chemists can symbolize the results of their analyses of many very complicated organic compounds, and can use them to direct synthetic procedures for preparing the compounds in the laboratory, linking one atom or group of atoms to another in a predictable way, step by step.

But sometimes the picture of localized bonding fails. Sometimes the chemical composition of a molecule and the spacial arrangement of its atoms do not dictate an unambiguous choice between two or more possible bonding schemes. In such a case there are two ways of modifying the picture of localized bonding.

One way is to examine molecular orbitals for the electrons that take all the atoms into account at once and not just in pairs. Then the bonding electrons can be pictured in states that are delocalized from any particular pair of atoms in the molecule. Such delocalization merely carries further the delocalization already visualized in forming the bond between two atoms. There the electrons are already removed from strict allegiance to the atoms and are shared between them.

This observation points to an analogy that suggests the second way of modifying the picture of localized bonding. As the last two chapters have shown, a good picture of the bond between two atoms can be made by examining the properties of the individual atoms. In a somewhat analogous way, a good picture can be made of the behavior of the ambiguously constructed molecules by thinking of their structures as combinations of alternative schemes of bonding, all taken at once - as mesomers of several simply linked structures. This device has the great advantage of preserving as well as possible the structural schemes that have proved to be so useful throughout chemistry.

The classic example of a molecule with an ambiguous structure is benzene, C_6H_6. All six carbon atoms, and all six hydrogen atoms, behave alike in chemical reactions, and any proposed bonding scheme must be consistent with that fact. In 1865 Friedrich Kekulé guessed that the carbon atoms are bonded together in a regular hexagonal ring, and that one hydrogen atom is bonded to each of them (Fig. 8.1a). The guess has since been confirmed: the ring is planar, and the hydrogen atoms are coplanar with the ring.

Since hydrogen has the valency one and carbon the valency four, a sat-

isfactory bonding scheme might be that shown in Fig. 8.1b. But the scheme is inconsistent with many chemical observations on benzene - with its chemical derivatives, for example, in which some of the hydrogen atoms are replaced by other atoms or groups of atoms. Three dichlorobenzenes can be prepared, which are distinguishable in melting point, boiling point, and the like. Their structures can be identified with those of Fig. 8.2a. But two different orthodichlorobenzenes have never been observed; and Fig. 8.2b shows that there should be two distinguishable compounds if the double bond were distinguishable from the single bond. In other sorts of compounds, double bonds are readily distinguishable from single bonds - they differ in length, for example (Fig. 7.13). Much evidence has conspired to force the conclusion that the bonds between the carbon atoms are all alike.

The only way to make these bonds look alike, and yet satisfy the valency of four for carbon, is to draw the structure shown in Fig. 8.3a, in which each carbon atom is singly bonded to a carbon atom across the ring. Interpreted literally, such a scheme is odd, for the distance across the ring is 2.8 Å and the usual single-bond distance between two carbon atoms is only 1.54 Å. The scheme is equally odd if it is interpreted as symbolizing a concentration of six bonding electrons near the middle of the ring, for the mutual repulsions in such an electronic concentration would assist the attractions of the carbon nuclei to spread the concentration out from the middle. The molecule is therefore regarded as a mesomer of a group of structures, of which the principal members are the two structures shown in Fig. 8.3b.

Sometimes chemists refer to such a combination as a "resonance combination." It is a poorly chosen term, but it has become deeply lodged in their speech about compounds like benzene. They mean that the wave functions for the electrons can be approximated by

a sum of the wave functions for those structures, in the way that Chapter 6 pictured the wave function for the hydrogen molecule as a sum of atomic wave functions.

Alternatively, the bonding can be pictured in terms of wave functions for an electron traversing all six carbon atoms, in the way that Chapter 5 displayed wave functions for an
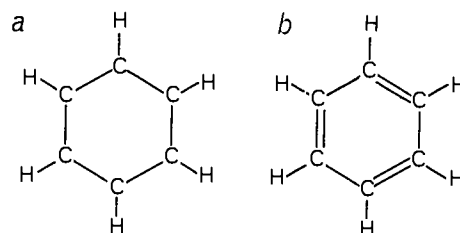

Fig. 8.1   In the molecule of benzene (a) all hydrogen atoms and all carbon atoms are coplanar. A bonding structure that satisfies the valency requirements is (b).
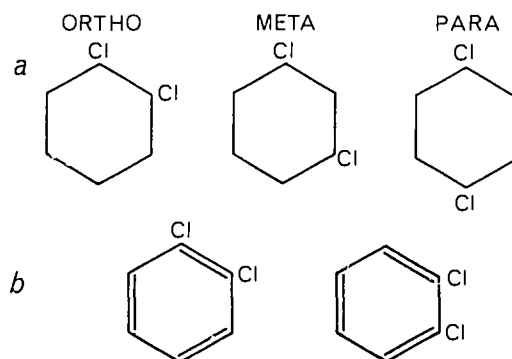

Fig. 8.2   Three distinguishable molecules (a) are ortho-, meta-, and paradichlorobenzene. Two distinguishable orthodichlorobenzenes (b) with the bonding sequences Cl-C-C-Cl and Cl-C=C-Cl have never been observed. Carbon atoms are at all corners of the hexagons.
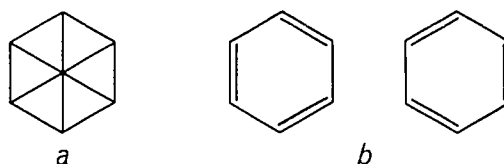

Fig. 8.3   The "Bamberger structure" (a) for benzene is less reasonable than a combination of two participating "Kekulé structures" (b).

electron in the presence of two attractive centers. For this purpose the benzene molecule would be visualized as in Fig. 8.4. Localized single bonds, between hydrogen atoms and carbon atoms, and between adjacent pairs of carbon atoms, employ three of the four bonding electrons of each carbon atom, and leave a total of six electrons to occupy the spacially extended orbitals.

Again a one-dimensional model, using delta wells to represent the atoms, provides a simple illustration of how the inquiry might proceed. The appendix to this chapter finds six independent wave functions, three "bonding" and three "antibonding," for the problem. The six electrons can occupy, by spin-opposed pairs, the three bonding orbitals. It turns out that the resulting collection of electronic states can have a lower energy than a collection of spacially localized bonds would have.

It is not surprising that the participation of different bonding structures is a common occurrence in molecules. When more than two nuclei are available to the electrons, it would be more surprising if the electrons did not use the additional space in which their potential energy is low to reduce their kinetic energy. The extent to which this happens, however, is restricted by the electronic behavior summarized in the exclusion principle. That behavior does not prevent all the electrons from occupy-
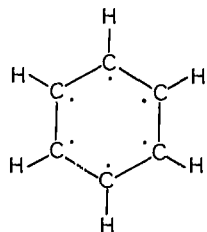

Fig. 8.4 The extended wave functions of the molecule of benzene must accommodate one electron from each carbon atom, left over after the other three electrons of principal quantum number 2 have been used to form localized bonds.

ing wave functions that are identical but in different positions in space. Insofar as the wave functions overlap, however, they will seldom be identical; some will have higher energy and some will have lower energy than localized wave functions would have. Thus it is not easy to predict what molecules will delocalize their electrons to a significant extent.

The experimental evidence for delocalized bonding comes from many properties of molecules of which perhaps the most important are (1) the geometrical arrangements of their component atoms, (2) their total energies, and (3) their dipole moments. The regular hexagonal configuration of benzene illustrates the first of these sorts of evidence. The second sort of evidence comes from thermochemical measurements - measurements of the heats absorbed and evolved in chemical reactions with other sorts of molecules. By suitable addition of those heats, the energies of the molecules can often be calculated. When delocalization is unimportant, it turns out that the energy of a molecule can be calculated as a sum of energies ascribed to its component localized bonds. Conversely, when the energy is lower than that, the difference can usually be ascribed to delocalization.

In the case of benzene the thermochemical value of the energy required to disperse the molecule into its component atoms is 1041.12 kcal per mole.[24] The energies required to break localized bonds, determined from experimental work on many molecules in which delocalization is negligible, are $E_{C-H} = 85.56$, $E_{C-C} = 62.77$, and $E_{C=C} = 101.16$ kcal per mole. If the benzene molecule had one of the Kekulé structures (Fig. 8.3b), the calculated energy would be $3E_{C-C} + 3E_{C=C} + 6E_{C-H} = 1005.15$ kcal per mole. The difference of 35.97 kcal per mole is called the "experimental value of the resonance energy" of benzene.

---

[24]See Discussion 3.1, Units.

Notice that the idea of "reson-
ance energy" is somewhat loose. It is
the amount by which the true energy
of the molecule is less than the en-
ergy that you think it would have if
its electronic structure corresponded
with some arrangement of localized
bonds. The arrangement of localized
bonds that you pick for comparison is
a best guess based on a knowledge of
chemistry, and usually chemistry
severely restricts the range of rea-
sonable guessing. The "resonance en-
ergy" remains as the difference be-
tween the true energy and that of
your best guess.

To see how the dipole moment can
give evidence of the importance of
delocalization in a molecule, turn to
a molecule very different from ben-
zene: nitrous oxide, N_2O, the "laugh-
ing gas" of anesthetic practice. Pay-
ing attention only to the valency
three of nitrogen and the valency two
of oxygen, one can propose for this
molecule the arrangement of bonds
shown in Fig. 8.5a. But the atoms in
the molecule are not triangularly ar-
ranged in fact; they are arranged in
a straight line in the order NNO. This
fact poses a problem in bonding that
offers a splendid opportunity to play
a game, dear to many chemical theor-
ists, in which electrons are pushed
about on paper to portray reasonable
bonding arrangements.

One possible arrangement is sug-
gested by the fact that the molecule
looks like a molecule of nitrogen
that has attached an atom of oxygen
at one end. In the nitrogen molecule
(Fig. 7.9) three of the five electrons
of principal quantum number 2 in each
nitrogen atom are exchanging places,
to form a triple bond, leaving two
electrons in each atom unexploited in
bonding. And an oxygen atom has an
unexploited 2p orbital that could ac-
commodate two electrons.

Suppose then that the so-called
nonbonding pair of electrons from a
nitrogen atom spend half their time
on the oxygen atom, and thus form a
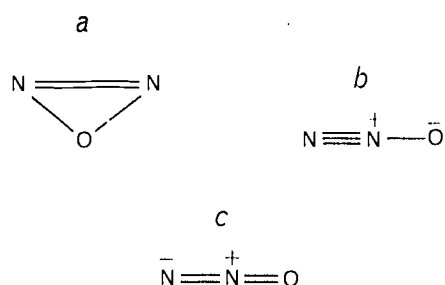bond. To assist its analysis, the

Fig. 8.5 For nitrous oxide, the structure
(a) is impossible because the molecule is
linear, and the structures (b) and (c) may
both participate because the dipole moment
of the molecule is almost zero.

formation of this bond could be re-
garded as taking place in two stages.
In stage No. 1 a nitrogen atom in the
molecule loses one electron to the ox-
ygen atom, and in stage No. 2 the re-
maining unpaired electron on the nitro-
gen atom exchanges with the new un-
paired electron on the oxygen atom to
form a single covalent bond. Stage No.
1 makes the nitrogen molecule into a
nitrogen molecule-ion of charge $+e$
and the oxygen atom into an oxygen ion
of charge $-e$. Stage No. 2 leaves these
net charges unchanged, and thus the
molecule would have a large dipole mo-
ment. Nitrogen atoms very frequently
form such "donor-acceptor" or "dative"
bonds. The proposed structure is dia-
gramed in Fig. 8.5b.

Now in fact, nitrous oxide has a
vanishingly small dipole moment. Hence
the proposed structure becomes credi-
ble only by supposing that it is ac-
companied by a participating structure
that cancels the dipole moment. It is
easy to believe that an equally im-
portant arrangement might be that dia-
grammed in Fig. 8.5c. There an elec-
tron is visualized as moving from the
central nitrogen atom to the other
nitrogen atom rather than the oxygen
atom. This structure can be regarded
as using one of the polar forms of
the nitrogen molecule to provide a
bond in which the oxygen atom has its
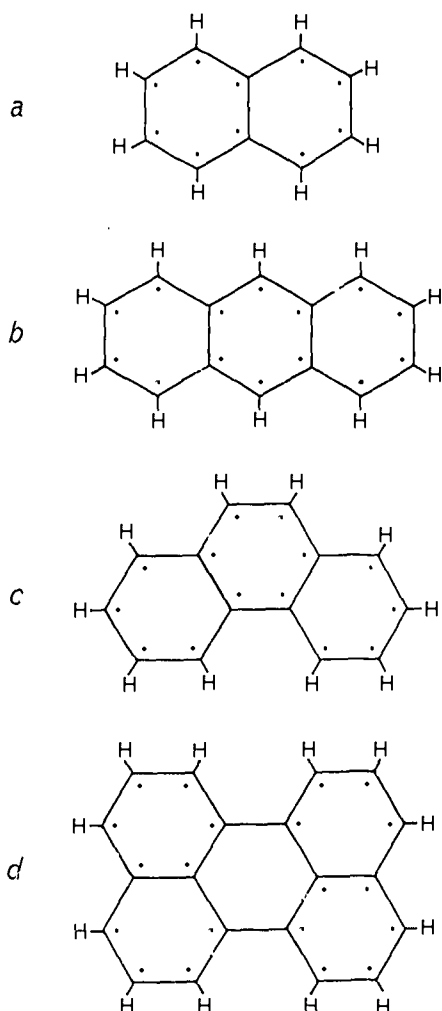usual valency of two. In fact nitrous

Fig. 8.6 The molecules of (a) naphthalene,
(b) anthracene, (c) phenanthrene, and
(d) perylene. Carbon atoms are at all cor-
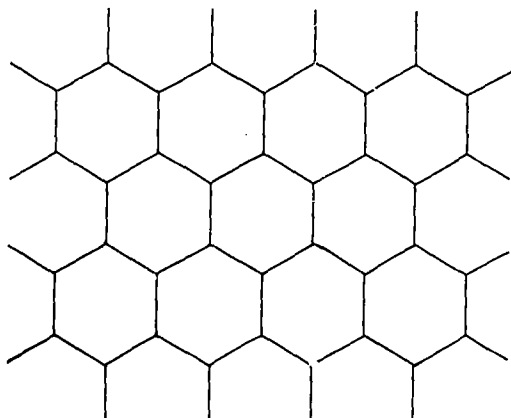ners and intersections in the diagrams.

Fig. 8.7   Graphite contains sheets of
"fused" benzene rings.

oxide is often described today as a
"resonance hybrid" of the structures
shown in Fig. 8.5b, c, with no net
dipole moment.[25]

There are many organic molecules
that resemble benzene in the type of
bonding that links their carbon atoms.
In the molecules (Fig. 8.6) of naphtha-
lene, anthracene, phenanthrene, and
perylene, for example, the electrons
not engaged in localized single bonds
are able to range over the entire
molecule. If benzene rings are fused
together in such a fashion as this in-
definitely, the structure in Fig. 8.7
arises; it is one plane of atoms in a
crystal of graphite. The electrons can
now range throughout the plane, and
indeed a single crystal of graphite
shows a relatively high electrical
conductivity in directions parallel to
the planes, and a relatively low con-
ductivity perpendicular to the planes.
These electrons, and those others that
form the localized single bonds, are
binding the carbon atoms together
tightly in the planes; the carbon-
carbon distance (1.42 Å) is like that
in benzene. Between the planes the
binding is largely by dispersion
forces, and the shortest carbon-
carbon distance is 3.4 Å.

Thus one can think of graphite as
a material that has gone part of the
way toward a metal. And there is an-
other way of looking at the behavior
of the relatively free electrons in
graphite that helps in visualizing
the bonding in metals. Consider the
free electrons in graphite - one
electron per atom - as trying to form
localized electron-pair bonds between
neighboring pairs of atoms. Count the
bonds per atom that the electrons try
to form, and compare that number with
the number of electrons per atom that
are available to form the bonds.

[25] Here the term "resonance" is especially inap-
propriate. The term refers to an analogy between,
on the one hand two similar oscillators that are
weakly coupled, and on the other hand two simi-
lar electronic states whose wave functions over-
lap. Here, however, the two states are not simi-
lar.

As Fig. 8.7 shows, each carbon atom has three nearest neighbors. Since each of the attempted bonds would connect two atoms, the number of such bonds per atom would be 3/2. If the bonds were localized electron-pair bonds, each would accommodate two electrons, and thus saturated bonding would use $2 \times 3/2 = 3$ electrons per atom. But there is only one of the free electrons available per atom. Hence these bonds are electron-deficient: the demand for electrons exceeds the supply.

Now make a similar count for an alkali metal, such as sodium. The alkali metals crystallize in a structure that gives to each atom eight nearest neighbors, and thus the number of bonds per atom is four. Since an alkali metal atom has only one electron in its outermost shell, the number of electrons available per atom is one, whereas eight would be needed to supply each bond with a pair of electrons. The large electron deficiency gives the electrons much freedom.

But the ideas of resonance and of electron-deficient bonding are not equivalent ideas: nitrous oxide is a good example of resonance without deficiency. The outermost electronic shell of each nitrogen atom - the shell with principal quantum number 2 - contains five electrons, and that of the oxygen atom contains six. In order to check the molecule for electron deficiency, these electrons can be paired off in the way shown in Fig. 8.8a, to suggest that some electrons stay on the atoms and some participate in localized electron-pair bonds. This scheme of pairing leaves two electrons, one on each extreme atom, to participate in a nonlocalized bond.

But if this were the true bonding structure, the system could make no distinction between one N-O bond and the other. It would pull the nuclei into a configuration symmetrical with respect to those two bonds, and there would be no electron deficiency in either. In short, the molecule would take the form of Fig. 8.5a.

Since the three atoms have in fact the linear arrangement NNO, the two electrons of the "nonbonding pair" on the central atom must participate in the bonding. This provides four electrons and two nearest-neighbor bonds for them to form, and again the counting scheme leaves no electron deficiency. But the electrons still cannot be paired in localized bonds, by such a scheme as that in Fig. 8.8b, because the scheme would require five electron pairs to find suitable orbitals on the central nitrogen atom. Four pairs of electrons use up the states with principal quantum number 2, and the fifth pair would be forced into a state of much higher energy, with principal quantum number 3.

Thus in the case of nitrous oxide either the idea of several participating states, or the idea of delocalized bonding such as Discussion 8.1 (see next page) describes, is essential to explain the properties of the molecule. As the properties of other molecules are measured in increasing diversity and with greater refinement, it is steadily becoming more evident that the idea of strictly localized covalent bonding is only a first approximation to the facts. When it is removed
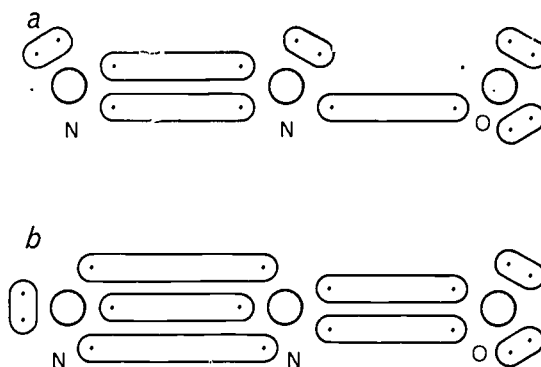

Fig. 8.8 In the electron-pairing scheme (a) for nitrous oxide, the two electrons left over would form a bond that would pull the molecule into the configuration of Fig. 8.5a. Scheme (b) would invoke a high-energy state on the central nitrogen atom.

Discussion 8.1

DELOCALIZED BONDS IN NITROUS OXIDE

In order to examine the states of delocalized electrons that participate in the bonding of nitrous oxide, seek wave functions that are appropriate to three attractive centers in a line.

Visualize removing four electrons, one from each of the extreme atoms and two from the central atom; then find wave functions in the field of the resulting ions; and finally put back the electrons one by one.

Thinking of the problem in one dimension, and approximating the ions by delta wells, you would look at the picture in Fig. 8.9. The two end wells are identical - an approximation suggested by the fact that the molecule has no dipole moment - and the central well is twice as deep as the end wells, because two electrons have been removed from the central atom.

You expect to find three wave functions, much as you found two for the case of two wells in Chapter 5. One of the functions will have no nodes, one will have one node, and one will have two nodes; and you expect that the corresponding energies will increase, becoming less negative, in

In the second of these functions you can see quite clearly a reflection of the picture that the idea of resonance also produced - the picture of polar states with extra electrons on the two extreme atoms. Squaring that

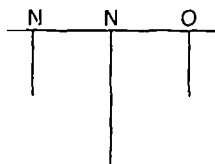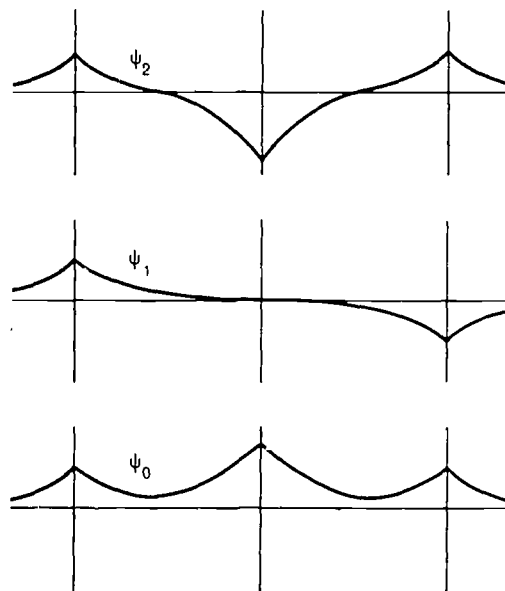Fig. 8.10 Expected form of wave functions for the wells of Fig. 8.9, with energies $E_0 < E_1 < E_2$.

Fig. 8.9 A scheme of delta wells to form a one-dimensional approximation for the wave functions of four bonding electrons in nitrous oxide.

that order. Since the problem is symmetrical about the central well, you can sketch the expected forms of the wave functions as in Fig. 8.10.

Now put back the four electrons. Two can go into the lowest-energy wave function and two into the function of next higher energy, leaving the highest-energy function unoccupied.

function makes clear that it represents a state in which the electron density is greatest at the extreme wells and vanishes at the central well. Of course the total electron-density distribution of the four electrons will be proportional to the sum of the squares of this function and the function of lowest energy, since those two represent the spacial dependence of the four occupied states. To answer whether that sum still reflects the special importance of polar states would require more detailed calculation.

from one atom, to participate in bonding with another, an electron has some probability, if only a small one, of finding itself anywhere within the molecule of which those atoms form a part.

PROBLEMS

8.1 Write the Kekulé structures of the molecules (Fig. 8.6) of naphthalene (three structures), anthracene (four structures), and phenanthrene (five structures).

8.2 Why can you not in principle determine the resonance energy of nitrous oxide relative to the structure of Fig. 8.5b by comparing a measured energy of nitrous oxide with the sum of the energy of the nitrogen molecule $E_{N \equiv N}$ and the energy E_{N-O} of the usual single bond between nitrogen and oxygen as found for example in such molecules as hydroxylamine, H_2NOH?

8.3 Use the electron-deficient bonding picture to explain qualitatively why the closest carbon-carbon distance in benzene is shorter than in graphite.

Appendix   A DELTA-WELL MODEL FOR BENZENE

A one-dimensional delta-well model for benzene can be constructed and studied in much the same way that the similar model for the hydrogen molecule-ion was studied in Chapter 5. Imagine six delta wells evenly spaced along one coordinate. In this case the system is cyclic, but if you imagine it to be cut at one point and spread out along a line, you can preserve its cyclic character in the calculation by matching the wave function at the end of the line to that at the beginning of the line.

It is helpful to use "local coordinates" in the problem, describing the wave function between each pair of wells by a coordinate whose origin is midway between the wells (Fig. 8.11). As in Chapter 5, the wave function for the coordinate x_j everywhere between its bounding wells will be

$$\psi_j = A_j e^{-kx_j} + B_j e^{kx_j}, \qquad (A8.1)$$

where A_j and B_j are constants and $k^2 \equiv -E$ is the energy. Matching ψ_j and ψ_{j+1} at the point where $x_j = R/2$ and $x_{j+1} = -R/2$, you obtain

$$A_j e^{-kR/2} + B_j e^{kR/2} = A_{j+1} e^{kR/2} + B_{j+1} e^{-kR/2}. \qquad (A8.2)$$

The discontinuity in derivatives across the delta well at the same point can be evaluated by the relations

$$\frac{d\psi_{j+1}}{dx_{j+1}}\bigg|_{x_{j+1} = -R/2} - \frac{d\psi_j}{dx_j}\bigg|_{x_j = +R/2} = -\eta \psi_j(R/2) \qquad (A8.3)$$
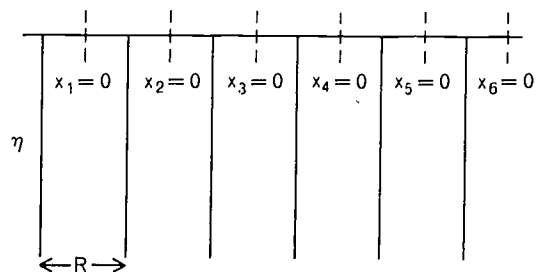

Fig. 8.11   A scheme of six similar delta wells, and local coordinates, to calculate the nonlocalized wave functions for a one-dimensional model of benzene.

where η is the parameter specifying the well:

$$-kA_{j+1}e^{kR/2} + kB_{j+1}e^{-kR/2} + kA_je^{-kR/2}$$

$$- kB_je^{kR/2} = -\eta(A_je^{-kR/2} + B_je^{kR/2}).$$

$$(A8.4)$$

Equations (A8.2) and (A8.4) are a pair which determine A_{j+1} and B_{j+1} in terms of A_j and B_j; they can be re-arranged to read

$$A_{j+1} = (\alpha+1)e^{-kR} A_j + \alpha B_j,$$

$$B_{j+1} = -\alpha A_j - (\alpha-1)e^{kR} B_j, \quad (A8.5)$$

where α denotes $\eta/2k$.

Rewrite Eqs. (A8.5), substituting

$j-1$ for j throughout, and then eliminate B_{j+1}, B_j and B_{j-1} from the four equations, to obtain a relation involving only the A's:

$$A_{j+1} + \left[(\alpha-1)e^{kR} - (\alpha+1)e^{-kR} \right] A_j$$

$$+ A_{j-1} = 0. \quad (A8.6)$$

This is a linear finite-difference equation in the independent variable j. Its solutions can be found by comparing it with the trigonometric identity,

$$\cos (j+1)\theta + \cos (j-1)\theta$$
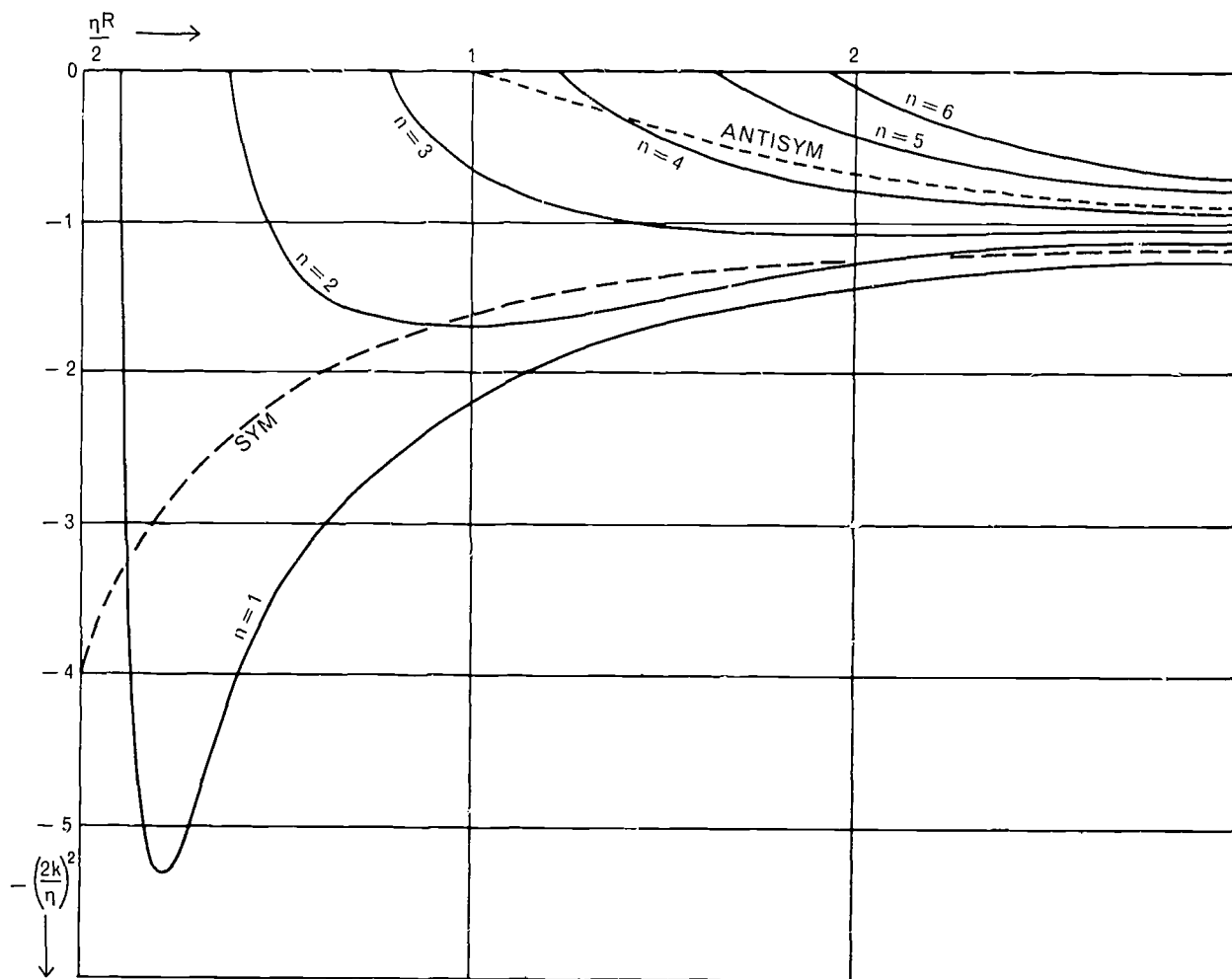
$$= 2 \cos j\theta \cos \theta. \quad (A8.7)$$

Fig. 8.12   Energy (vertically) versus bond length (horizontally) in the six wave functions of the one-dimensional cyclic delta- well model for benzene. Dotted lines are the energies of the wave functions for two delta wells (Fig. 5.8).

Clearly its solutions can be taken as

$$A_j = A \cos j\theta, \qquad (A8.8)$$

where

$$\cos \theta = \tfrac{1}{2} \left[(\alpha+1)e^{-kR} - (\alpha-1)e^{kR} \right]$$

$$\equiv \cosh kR - \alpha \sinh kR. \qquad (A8.9)$$

The cyclic condition must now be applied to this solution. That condition requires that the A's and B's repeat themselves at the seventh set $(A_7 = A_1, B_7 = B_1)$ and this is accomplished in the solution (A8.8) by requiring

$$\theta = \frac{n\pi}{7}, \qquad (A8.10)$$

where n is any integer. All the distinct solutions are provided by n = 1, 2,3,4,5,6; the solutions for larger values of n only duplicate these. Thus there are six independent wave functions for the system of six wells, just as there are two - the symmetric and antisymmetric functions - for the two wells used in discussing the hydrogen molecule-ion.

The energy corresponding to each of these wave functions can be obtained from Eq. (A8.9). For each value of n in Eq. (A8.10) for θ, Eq. (A8.9) gives k, and thus the energy $E = -k^2$, as a function of the interatomic separation R and the nature of the atom, η. Fig. 8.12 plots the roots of this equation, and shows as dotted lines the roots of the corresponding equation (Chapter 5, Eq. (A5.9) for the wave functions for two wells.

Notice that, alike in the two-well and the six-well cases, half the wave functions have energies that decrease and half have energies that increase with decreasing separation of the wells: half are "bonding" functions and half are "antibonding" functions. The fact that all the energies in the six-well case become infinite for very small R reflects an artificiality of the model. Since the model is cyclical and one dimensional, it shrinks the space available to the
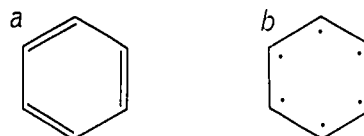

Fig. 8.13 The "resonance energy" of benzene is the difference between the energies of the molecule when six of its electrons are engaged (a) in localized and (b) in nonlocalized bonding.

electrons as R decreases. There is no way for an electron to increase its de Broglie wavelength and thus decrease its kinetic energy by spending more time away from the space between the wells, as there is in the open-ended model of two wells. The real three-dimensional case would not afford such minima in the electronic energy as this model exhibits.

The actual interatomic spacing R in molecules like benzene, however, is sufficiently large to make this defect of the model negligible. Thus it is significant to compare the energy of six electrons in the cyclical model with the energy they would have if they were in localized bonds of the same length. You can think, for example, of comparing the energies of the two structures of Fig. 8.13 for benzene.

Since the scale in Fig. 8.12 is in atomic units, using the reduced variables $\eta R/2$ and $-(2k/\eta)^2$, it gives energies and distances directly in atomic units for hydrogen, whose 1s state can be represented by a well with $\eta = 2$. You can determine a suitable value for a well to represent a 2p state of carbon by taking $\eta = 2\sqrt{I_C/I_H}$, where I_C/I_H is the ratio of the first ionization potentials of carbon and hydrogen: $I_H = 13.59$ eV, $I_C = 11.27$ eV, $I_C/I_H = 0.828$. Neglecting the electrostatic interactions of the electrons with one another but bearing in mind the exclusion principle, you can calculate for various values of R the energy of two electrons (of opposite spin) in each of the three lowest-energy six-well wave

functions, add them, and compare the
result with six times the energy in
the symmetric two-well function of
Chapter 5, plotted again in Fig. 8.12.
Over a large range of R the difference
turns out for carbon to be about 0.1
atomic unit = 1.35 eV = 31 kcal per

mole in favor of the cyclical bonding.
This difference corresponds well with
the difference of 34.4 kcal per mole
that has been found by inference from
the heats of combustion of organic
compounds. Chemists call it the
"resonance energy" of benzene.

PROBLEMS

8.4 Show that the wave functions for
the cyclical set of six delta
wells have $n - 1$ zeros.

8.5 Show that the solid curves in Fig.
8.12:

(a) have their zeros of energy at
$\eta R/2 = 1 - \cos (n\pi/7)$;

(b) pass through the value
$(2k/\eta)^2 = 1$ (the value of the
asymptotic line) at $\eta R/2 = \log$
$\sec (n\pi/7)$;

(c) have minima whose values are
$(2k/\eta)^2 = \operatorname{cosec}^2 (n\pi/7)$ for the
first three values of n.

8.6 There is a way to think about Eqs.

(A8.5) that has attractive mathe-
matical elegance. Think of A_j and
B_j as the Cartesian components of
a vector $\vec{R}_j$ in a two-dimensional
"space." Then think of Eqs. (A8.5)
as embodying an "operation" T that
transforms the vector $\vec{R}_j$ into the
vector $\vec{R}_{j+1}$. Finally think of the
cyclic property of the system un-
der study as requiring that six
successive performances of the
operation carry the vector to
identity with the initial vector;
in other words, $T^6 = I$, where I
is the identity operation. Embody
these ideas in a program that de-
rives the results obtained by the
use of finite-difference equations
in the appendix.

Our study of bonding could continue indefinitely, refining our calculations, specializing them to interesting cases, and examining the results of applying increasingly sophisticated tools for studying molecules experimentally. Instead of pursuing that route, stand back to consider the insights gained by this brief inquiry into the nature and variety of the bonds between atoms.

Surely the most important insight is the realization that a quarter millenium of experiment and reflection has accomplished Sir Isaac Newton's Business. By ascribing to interatomic bonds an electrostatic explanation, a good account can be given of the bonds so far encountered, in all their variety. To encompass by a single explanation so great a span as that separating the vapor of salt and a crystal of diamond is a remarkable vindication cf Occam's razor, "Let not hypotheses be multiplied beyond the necessity to explain the facts."

Behind this unity is still hidden some diversity, of course. We have taken for granted the existence of many sorts of massive nuclei with differing amounts of positive charge, and the existence of a single sort of relatively light electrons. We have taken for granted that the positive charge comes in units equal in size, though opposite in sign, to the charge on the electron. Moreover, by finding that in interatomic bonding the gravitational forces are negligible compared with the electrostatic forces, we have suppressed the disunity implicit in our present inability to find a relationship between these two sorts of forces. Nevertheless there can be much satisfaction in having found a common explanation for so wide a variety of occurrences as that of the bonds between atoms.

Despite their common origin, how-ever, their variety is sufficient to suggest the convenience of classifying bonds in the way developed in Chapter 2. Subsequent chapters have amplified the meanings of those classifications, and quantified their terms, sufficiently to make profitable another survey of how the materials of the world fit into them.

It is interesting, for example, to compare the bonding of atoms in the worlds of the living and the inanimate. Living matter is made of "organic compounds," and their great diversity is accountable to the unique ability of carbon atoms to bond covalently to one another. Each molecule of an organic compound is built upon a skeleton of carbon atoms tightly bonded in rings and branching chains. Most of the links in these chains are localized electron-pair bonds, hybridized in the ways described at the end of Chapter 7. The hydrogen atoms, and occasionally also atoms of oxygen and nitrogen, are tied to the skeleton, again by covalent bonds. The chainlike structure of the hydrocarbon n-octane (Fig. 9.1) exemplifies the simplest sort of organic compound.
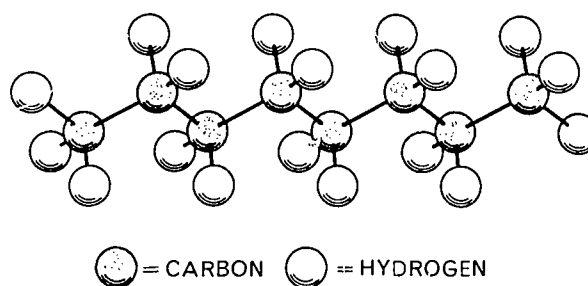

$\bigcirc$ = CARBON $\bigcirc$ = HYDROGEN

Fig. 9.1 The chain of carbon atoms in the hydrocarbon, n-octane (C_8H_{18}), linked by sp^3 bonds, exemplifies the simplest type of organic compounds. This and the succeeding diagrams of molecules are not drawn to scale. They are intended only to show the bonding connections between the atoms, and some of the spacial relations which those connections imply.
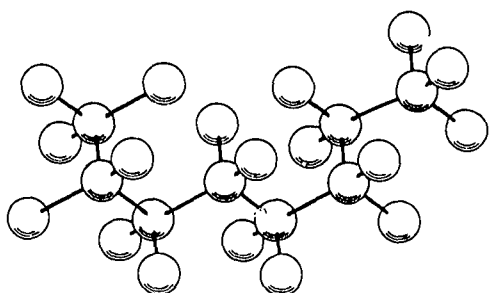
Fig. 9.2 Even though the bond angles and bond lengths are fixed in n-octane, groups of atoms can rotate freely about any C-C bond, as long as they do not get in one another's way.
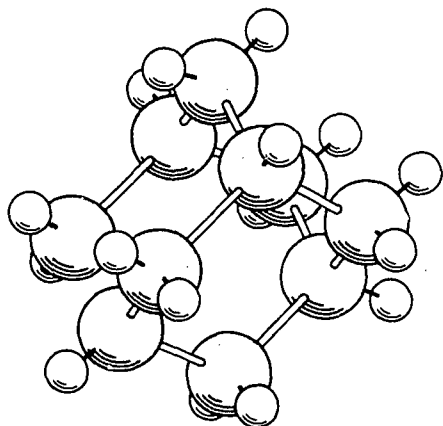

Fig. 9.3 In the hydrocarbon, adamantane $(C_{10}H_{16})$, the pattern of sp^3 bonding restrains the atoms quite rigidly.

Since oxygen and nitrogen atoms are more electronegative than carbon, their bonds to carbon atoms have an ionic ingredient. That ingredient gives the molecules local dipole moments, whose interaction with the similar dipole moments in neighboring molecules makes the molecules cohere.

The links in such a chain as that shown in Fig. 9.1 are made of sp^3 hybrid bonds; and since such a bond is cylindrically symmetrical about its axis, groups of atoms can rotate about any of those bonds. Hence, even though the bond holds its two atoms quite tightly at a fixed distance, and stands quite rigidly at the tetrahedral angle to the other three bonds

formed by the same atom, the molecule as a whole has considerable flexibility (Fig. 9.2). Certainly in a vapor of such a material, and probably even in its liquid form or in solution, the molecules are constantly flexing and coiling with internal thermal motions. In the solid form of such a substance, the molecules will adopt the positions and shapes that enable them to pack together most closely under the influence of the weak van der Waals forces that bond them to one another. But since the molecules remain flexible, solid organic materials are often soft and pliant.

In some organic compounds, however, the linking within each molecule is so patterned that no flexibility is left: the requirements that the bonds have constant lengths and stand at tetrahedral angles constrain all the atoms to fixed relative positions about which they can only quiver. Diamond (Fig. 2.3), in which carbon atoms are bonded by sp^3 bonds, is a conspicuous example of the resulting rigidity. For the same reason the molecules of the hydrocarbon, adamantane (Fig. 9.3), behave much like inflexible spheres.

In making the modern plastics this principle is used to provide the desired degree of stiffness. Many plastics are based upon molecules whose skeleton is an extremely long chain of carbon atoms. Polythene, for example, consists of hydrocarbon molecules like those of n-octane in which the chain (Fig. 9.4) contains several hundred carbon atoms instead of eight. Rubber, though a more complicated structure, is essentially similar. The art of vulcanizing rubber is in large part the art of cross-linking these chains (Fig. 9.5) in order to decrease their flexibility. The links, made by introducing sulfur atoms, can be multiplied to the number producing "hard rubber," in which the flexibility of the original rubber has nearly vanished. The vulcanizing art appeared long before an explanatory theory of cross-linking, but now that theory can

be used to provide directives for the design of molecules that can be deliberately cross-linked to any desired extent.

In another important class of plastics, including nylon, the skeletal chain is made partly of nitrogen atoms, and one of the carbon atoms adjacent to each nitrogen atom bears an oxygen atom closely bonded to it, as Fig. 9.6 shows. Because of the differences in the electronegativities of carbon, nitrogen, and oxygen, the covalent bonds in this part of the molecule have large ionic ingredients that produce a local dipole moment. The isolated dipole moments along the chain interact with the dipole moments in adjacent chains to provide cross-linkings which, though weaker than those of covalent bonds, are stronger than the dispersion forces that hold together the molecules of a hydrocarbon. The total strength of the force holding molecule to molecule can be controlled by spacing the dipolar atomic groups suitably along the chain.

There is another way of controlling the strength of the intermolecular forces in these nitrogen-bearing plastics - a way that gives insight into some of the properties of the proteins that compose the flesh and muscle of animals. The forces can be weakened by attaching short side chains to the principal chain of the molecular skeleton and so holding the dipoles in adjacent skeletons further apart.

In the skeletal chain of the proteins, each pair of units that contribute a local dipole moment - the
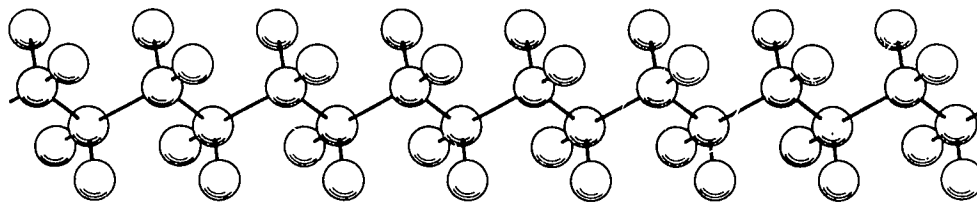

Fig. 9.4 A molecule of the modern plastic, polythene $(CH_2)_n$, consists of a chain like that shown in Fig. 9.1, continued through several hundred atoms.

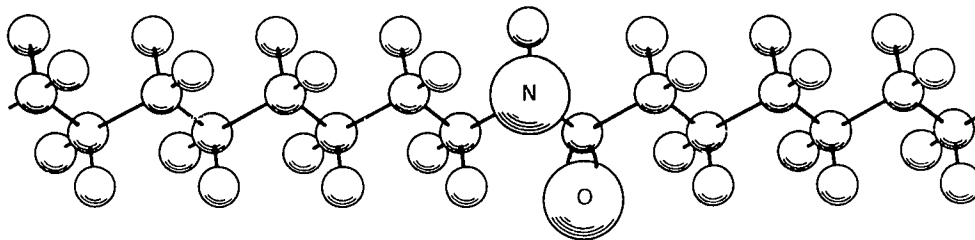Fig.9.5 Cross-linking long molecular chains by covalent bonds increases rigidity of a plastic.

Fig. 9.6 In plastics of the polyamide type, the skeletal chain acquires local dipole moments at the points where the (NH) - (CO) configuration occurs.
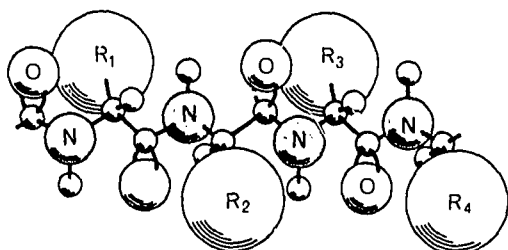
Fig. 9.7 A protein is a polyamide with closely spaced (NH) - (CO) configurations and with side groups that vary in nature and size. Typical groups are H-, $(CH_3)_2 CH \cdot CH_2-$, and $HO \cdot C_6H_4-CH_2-$.

NH and CO units - is separated from the next pair by only one carbon atom. But each of those carbon atoms carries a relatively large side group (Fig. 9.7). The side groups vary in nature from one protein to another, and they also vary from point to point
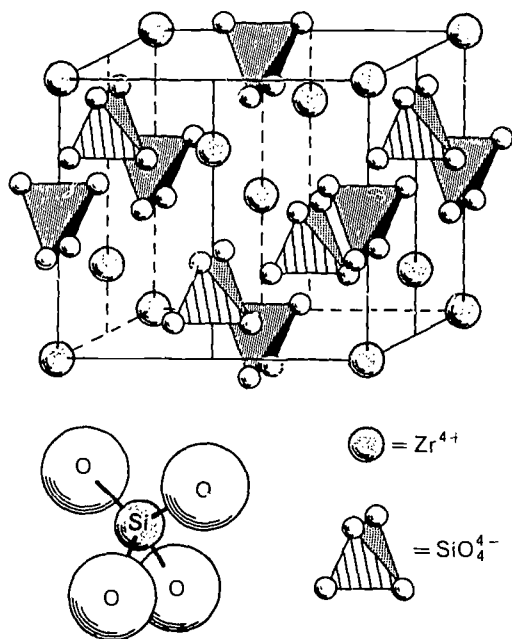
along the principal chain of any one molecule. Some of these side groups are simple chains, others are rings. Thus the strong attractions between the numerous dipoles are weakened in ways that have much subtle variety, and the varying shapes of the side groups impose additional variety on the ways in which any of the molecules can coil within itself and can pack together with its fellow molecules.

Turning from the organic world, dominated by compounds of carbon, we find the inorganic world dominated by compounds of silicon. At first one might expect to find silicon playing precisely the part of carbon. It falls directly beneath carbon in the same column of the periodic table, and it has four bonding electrons that could form hybrid bonds. In fact, however,

Fig. 9.8 The SiO_4 group takes a central position, as a structural base in the inorganic world, that is somewhat analogous to the position of the carbon atom in the organic world. In some minerals (for example, zircon) it stands as a tetravalent ion, here shown as a tetrahedron with corner oxygens.
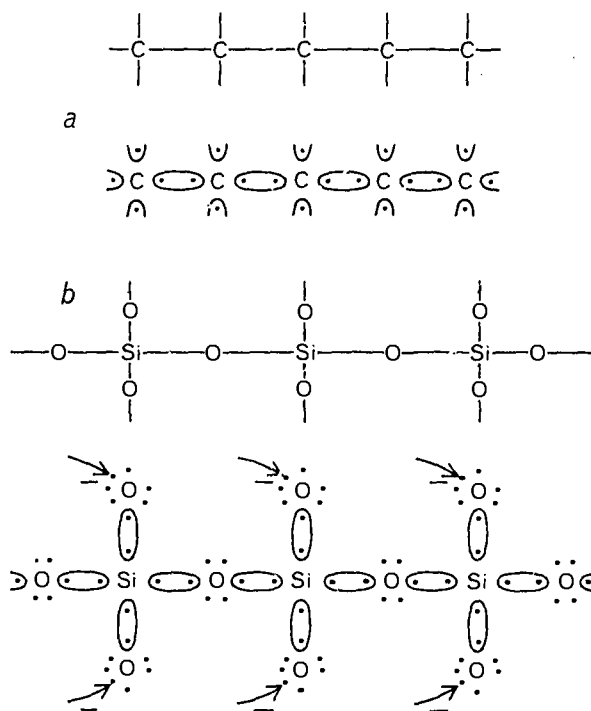

Fig. 9.9 In most organic compounds, the carbon skeletons (a) are clothed by covalently bonded atoms, so that the molecules are held to one another by van der Waals forces. In most minerals, the silica skeletons (b) bear a net negative charge, and the minerals are held together by the ionic forces between skeletons and positive ions.

two silicon atoms never bond to each other directly in a mineral. Each silicon atom is bonded directly to four oxygen atoms by sp^3 bonds. One can picture each silicon atom at the center of a tetrahedron whose corners are occupied by oxygen atoms.

In isolation such a tetrahedron has a strong electron affinity. Since the bond to the silicon atom employs only one of the bonding electrons of an oxygen atom, there is room in each for one more electron in an atomic orbital of principal quantum number 2. Hence an isolated SiO_4 group readily forms the negative orthosilicate ion, SiO_4^{4-} (Fig. 9.8).

More often, however, one finds silicon atoms bonding to one another through oxygen bridges: a bridging oxygen atom forms covalent bonds with two silicon atoms. In the resulting structures one can find interesting analogies to organic compounds. For example, a chain of the form $-Si-O-Si-O$ bears some resemblance to a chain of the form $-C-C-$.

But as Fig. 9.9 points out, the carbon skeleton, by clothing itself with covalently bonded atoms, becomes electrostatically neutral. In the silicate skeleton, on the other hand, the oxygen atoms that are not engaged in bridging, acquire electrons so that the entire skeleton becomes a negative ion. In a mineral those electrons are contributed by metal atoms which thus become positive ions. In the mineral diopside equal numbers of calcium and magnesium atoms furnish the metal ions. The entire mineral is held together, therefore, by ionic bonds whose strength greatly exceeds that of the van der Waals forces holding the organic solids together. The positively charged metal ions distribute themselves among the negatively charged silicate skeletons in whatever manner their sizes and the ionic forces make most favorable.

Often the Si-O-Si-O- links form rings or sheets instead of chains. In the mineral benitoite, rings are closed by three SiO groups, and each
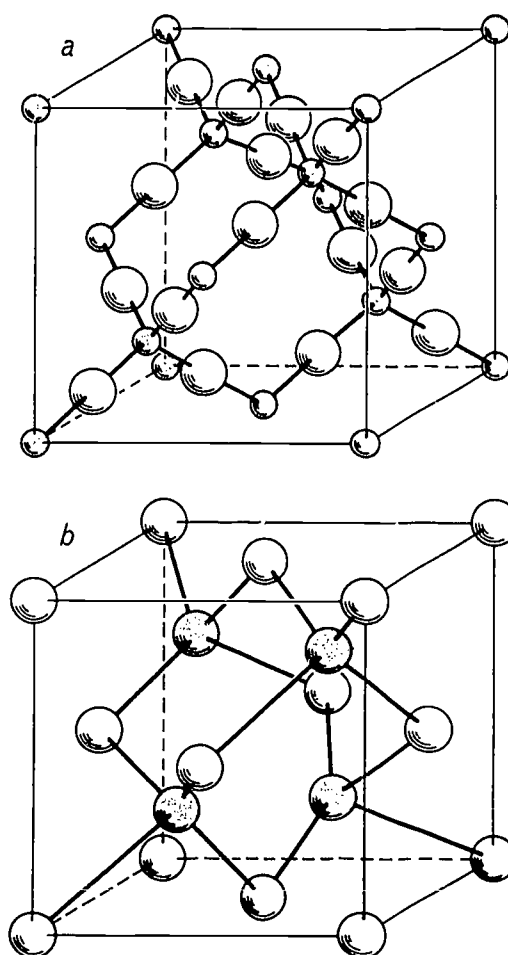

Fig. 9.10 In cristobalite (a) oxygen atoms form bridges between silicon atoms that are arranged in the same way as the carbon atoms in diamond (b).

ring is accompanied by a barium ion and a titanium ion. In beryl a ring of six SiO groups accommodates three beryllium ions and two aluminum ions. Just as in sodium chloride, it is impossible to identify molecular units in these minerals; one can identify only ionic units.

But, just as among the compounds of carbon, one can find among the minerals instances in which the skeleton is tightly cross-linked. Compare, for example, the crystal structure of diamond with that of cristobalite, one of the many structures adopted by silicon dioxide whose more usual structure is quartz. As Fig. 9.10 shows,

the silicon atoms occupy sites that form a diamondlike structure opened out by the bridging oxygen atoms.

From the complicated structures of the proteins and the minerals, turn finally to look at one of the simplest molecules, H_2O - a molecule that covers deeply three quarters of the earth's surface and moistens much of the rest. Despite its apparent simplicity, it behaves in many mys-

terious ways. But its behavior can be partly understood in terms of bonds discussed in the foregoing chapters.

One of the most conspicuous properties of water is that it <u>wets</u>: in other words, water molecules stick to most other molecules quite tightly. For helping to explain this property, we can make with our bonding pictures an argument running as follows. Since oxygen atoms are electronegative, their bonds to hydrogen atoms have a large ionic ingredient, as you noticed in Figs. 7.7 and 7.8. Since the two bonds are not collinear but stand at an angle of 105°, their ionic ingredients give the water molecule a large dipole moment. When a water molecule comes close to a molecule of another sort, the electric field due to its dipole moment (Fig. 4.2) induces a dipole moment in the neighboring molecule, oriented in an attractive direction.
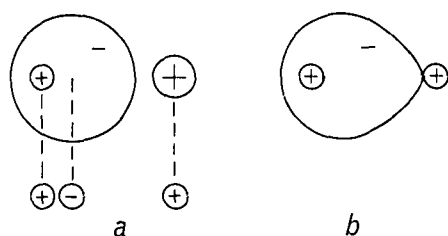

Fig. 9.11   A positive ion induces a dipole moment (a) in a neutral atom, oriented in an attractive sense. Since a proton is the smallest positive ion, it can come closest to the electron cloud of another atom (b), and stick fairly tightly to it.

But in the magnitude of its wetting affinity, water shows a larger variation that this argument can explain. It shows an especially strong affinity for oxygen-bearing molecules. Indeed it wets wood and paper, whose cellulose molecules expose many oxygen atoms at their surfaces, almost irresistibly.

Here the especially strong polarizing force of protons is at work. Recall, with the aid of Fig. 9.11, that a positive ion will induce in a neighboring neutral atom a dipole moment that is oriented in an attractive sense. The smaller the positive ion is, the nearer it can get to the electron cloud of the neutral atom, and hence the stronger will be the attraction it establishes. A proton is much the smallest of positive ions, and it can get stuck quite tightly to neutral atoms. When those are atoms of oxygen, and the proton forms part of a water molecule in which it is already attached to another oxygen atom, the proton can pull the two oxygen atoms together and bond itself almost even-handedly to both.
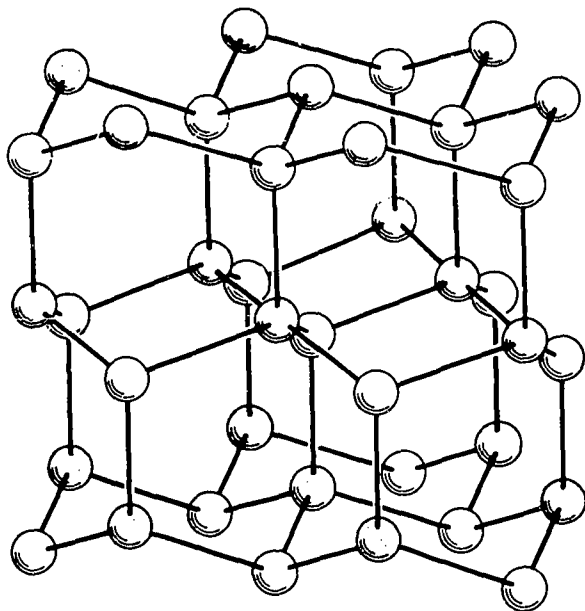
Not quite even-handedly, of

Fig. 9.12   Along the line between each neighboring pair of oxygen atoms in ice is one hydrogen atom. Most of the time it is nearer to one or the other of the oxygen atoms, and most of the time each oxygen atom has two hydrogen atoms near it.

course, since the oxygen atom in its parent water molecule is negatively charged and attracts it more strongly than a neutral atom. In molecules such as cellulose, however, the exposed oxygen atoms are also negatively charged. Bonds of the type exemplified by water and cellulose are often called hydrogen bonds. Sometimes it requires as much as 0.3 eV to break such a bond.

Clearly ice is the perfect candidate for hydrogen bonding: the protons should find its oxygen atoms indistinguishable. Actually the atomic arrangement in ordinary ice - other forms of ice can be produced at high pressures - is the cage-like structure whose oxygen ions are shown in Fig. 9.12. One proton is located somewhere along each of the bonding connections, and at any one time each oxygen ion has two protons near it. But each oxygen ion has four equivalent bonding connections, and the protons switch their allegiance from one oxygen ion to another along those connections. No wonder a glacier can slowly flow!

But much of the behavior of ice still remains unexplained. Consider a snowflake, its branches replicating one another in six-fold symmetry - differently in each flake. How does it communicate, at each instant, through millions of interatomic distances, its next instant's growth plan? We do not know; the flake is one of the world's tiny beauties, and one of its large mysteries.

PROBLEMS

9.1 If there is an "organic" world where silicon atoms (not SiO_4 groups) replace carbon atoms in proliferating "organic compounds," would you expect to find it in a hotter or a colder environment than that provided by the Earth?

9.2 Would you attach any significance to the fact that almost all the carcenogenic (cancer-producing) hydrocarbons known at present are "benzenoid," or in other words have bonding schemes in which the electrons are delocalized in the ways described in Chapter 8?

9.3 Protons differ from electrons primarily in having an opposite charge, and a mass about 2000 times greater; but their "sizes" are nearly the same. Discuss the problems, arising from the bonding properties of hydrogen atoms, that would afflict the development of a "protonics industry," comparable with the electronics industry, in which these tiny charged particles are exploited to perform comparably useful duties.